

Elements of Ensemble Theory

In 1902 Gibbs, one of the founders of Statistical Mechanics, introduced the concept of ensemble (a French word meaning assembly of systems). **An ensemble is a collection of essentially independent systems, which are macroscopically identical but microscopically different.**

Three types of ensemble are important in statistical mechanics. The classification depends on the matter in which the systems interact.

2.1 MICROCANONICAL ENSEMBLE

The microcanonical ensemble is a collection of independent systems, having the **same number of particles N , volume V and an energy between E and $E + \delta E$** . So the individual systems of a microcanonical ensemble are separated by rigid, impermeable and insulated walls, such that the values of E , V and N for a particular system are not affected by the presence of other systems. Thus, **in microcanonical ensemble, neither energy nor matter is exchanged.**

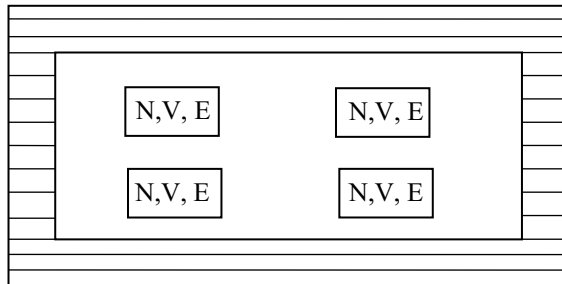


Fig. 2.1. Microcanonical ensemble.

Now

$$E = \frac{1}{2m} \sum_{i=1}^N \vec{p}_i^2 = \frac{1}{2m} \sum_{i=1}^N \sum_{\alpha=1}^3 p_{i\alpha}^2$$

$$\Rightarrow 2mE = \sum_{i=1}^N \sum_{\alpha=1}^3 p_{i\alpha}^2 \quad (2.1.9)$$

where $\vec{p}_i^2 = p_{i1}^2 + p_{i2}^2 + p_{i3}^2$, denoting x, y, z components by 1, 2, 3 respectively.

Obviously, the sum contains $3N = f$ square terms ($f = \text{degrees of freedom}$). For $E = \text{constant}$, it describes a sphere of radius $\zeta(E) = (2mE)^{\frac{1}{2}}$ in the f -dimensional space of the momentum coordinates. Hence $\Omega(E)$ is proportional to the volume of phase space contained in the spherical shell lying between the sphere of radius $\zeta(E)$ and that of slightly larger radius $\zeta(E + \delta E)$.

We now calculate the volume of the N -dimensional sphere. From the dimensional analysis, the volume of a N -dimensional sphere is

$$W_N = C_N \zeta^N \quad (2.1.10)$$

where C_N is a constant and is given by

$$C_N = \frac{\pi^{\frac{N}{2}}}{\Gamma(\frac{N}{2} + 1)} \quad (2.1.11)$$

(see Appendix II).

Using (2.1.11) in (2.1.10), the volume of the N -dimensional sphere becomes

$$W_N = \frac{\pi^{\frac{N}{2}}}{\Gamma(\frac{N}{2} + 1)} \zeta^N \quad (2.1.12)$$

Hence, the volume of the $3N$ -dimensional sphere of radius $\sqrt{2mE}$ is

$$W_{3N}(E) = \frac{\pi^{\frac{3N}{2}}}{\Gamma(\frac{3N}{2} + 1)} (2mE)^{\frac{3N}{2}} \quad (2.1.13)$$

$$\therefore \Omega(E) = \frac{V^N}{h_0^{3N}} \frac{\partial W_N(E)}{\partial E} \delta E$$

$$\Rightarrow \Omega(E) = \left(\frac{2m\pi}{h_0^2} \right)^{\frac{3N}{2}} \frac{V^N}{\Gamma(\frac{3N}{2})} E^{\frac{3N}{2}} \delta E \quad (2.1.14)$$

Neglecting 1 compared to N

$$\Omega(E) = \Omega_E \delta E = \left(\frac{2m\pi}{h_0^2} \right)^{\frac{3N}{2}} \frac{V^N}{\Gamma(\frac{3N}{2})} E^{\frac{3N}{2}} \delta E \quad (2.1.15)$$

Since $3N = f$, we see that

$$\Omega(E) \sim E^f \quad (2.1.16)$$

N is of the order of Avogadro's number and so very large. **Thus, $\Omega(E)$ is an extremely rapidly increasing function of the energy E of the system.**

The entropy of the ideal gas is

$$\begin{aligned} S &= k \ln \Omega_E \\ &= Nk \ln \left[\frac{2m\pi E}{h_0^2} \right]^{\frac{3}{2}} + Nk \ln V - k \ln \Gamma \left(\frac{3N}{2} \right) \end{aligned} \quad (2.1.17)$$

Now $\Gamma \left(\frac{3N}{2} \right) = \left(\frac{3N}{2} - 1 \right)! = \frac{3N}{2}!$, since $N \gg 1$.

Again by Stirling's approximation

$$\begin{aligned} \ln \frac{3N}{2}! &= \frac{3N}{2} \ln \frac{3N}{2} - \frac{3N}{2} \\ &= N \ln \left(\frac{3N}{2} \right)^{\frac{3}{2}} - \frac{3N}{2} \\ \therefore \ln \Gamma \left(\frac{3N}{2} \right) &\cong N \ln \left(\frac{3N}{2} \right)^{\frac{3}{2}} - \frac{3N}{2} \end{aligned} \quad (2.1.18)$$

Using (2.1.18) in (2.1.17)

$$\begin{aligned} S(E, V) &= Nk \ln \left[\frac{2m\pi E}{h_0^2} \right]^{\frac{3}{2}} + Nk \ln V - Nk \ln \left(\frac{3N}{2} \right)^{\frac{3}{2}} + \frac{3}{2} Nk \\ \Rightarrow S(E, V) &= Nk \ln \left[V \left(\frac{4m\pi E}{3h_0^2 N} \right)^{\frac{3}{2}} \right] + \frac{3}{2} Nk \end{aligned} \quad (2.1.19)$$

Solving for E in terms of S and V , we obtain the internal energy given by

$$E(S, V) = \left(\frac{3}{4\pi} \frac{h_0^2}{m} \right) \frac{N}{V^{\frac{2}{3}}} \exp \left(\frac{2}{3} \frac{S}{Nk} - 1 \right) \quad (2.1.20)$$

Again from thermodynamics

$$TdS = dE + PdV \quad (2.1.21)$$

Then the temperature is given by

$$T = \left(\frac{\partial E}{\partial S} \right)_V = \frac{2}{3} \frac{E}{Nk} \quad (2.1.22)$$

Hence, the specific heat at constant volume is given by

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V = \frac{3}{2} Nk \quad (2.1.23)$$

From (2.1.21), the pressure P is given by

$$P = - \left(\frac{\partial E}{\partial V} \right)_S = \frac{2}{3} \frac{E}{V} \quad (2.1.24)$$

Using (2.1.22) in (2.1.24), we finally get

$$P = \frac{NkT}{V} \Rightarrow PV = NkT$$

This is the equation of state of the ideal gas.

PROBLEM 2.1: Consider an isolated system consisting of a large number N of weakly interacting localized particles of spin $1/2$ in an external magnetic field H . Each particle has a magnetic moment μ , which can point either parallel or anti-parallel to the field H . Consider the energy range between E and $E + \delta E$ where δE is very small compared to E but microscopically large so that $\delta E \gg \mu H$. What is the total number of states $\Omega(E)$ lying in this energy range? Hence, find the temperature T .

SOLUTION

Let n be the number of spins aligned parallel to \vec{H} . So $(N - n)$ is the number of spins aligned anti-parallel to \vec{H} .

\therefore The total energy of the system is

$$\begin{aligned} E &= -n\mu H + (N - n)\mu H \\ &= N\mu H - 2n\mu H \end{aligned}$$

$$\Rightarrow n = \frac{N}{2} - \frac{E}{2\mu H} \quad (\text{i})$$

Then, if the energy of the system is exactly E , the number of accessible microstates is

$$\Omega_E = {}^N C_n = \frac{N!}{n!(N-n)!} = \frac{N!}{\left(\frac{N}{2} - \frac{E}{2\mu H}\right)! \left(\frac{N}{2} + \frac{E}{2\mu H}\right)!} \quad (\text{ii})$$

where we use equation (i).

From equation (i), $\delta n = \frac{\delta E}{2\mu H}$ (considering magnitude only).

Hence, the total number of states in the range E to $E + \delta E$ is

$$\Omega(E) = \Omega_E \delta n = \frac{N!}{\left(\frac{N}{2} - \frac{E}{2\mu H}\right)! \left(\frac{N}{2} + \frac{E}{2\mu H}\right)!} \cdot \frac{\delta E}{2\mu H} \quad (\text{iii})$$

From equation (1.22.10) the temperature T is defined through the relation

$$\frac{1}{kT} = \frac{\partial \ln \Omega}{\partial E} \quad (\text{iv})$$

Taking logarithms on both sides of equation (ii)

$$\ln \Omega = \ln N! - \ln \left(\frac{N}{2} - \frac{E}{2\mu H}\right)! - \ln \left(\frac{N}{2} + \frac{E}{2\mu H}\right)! \quad (\text{v})$$

Using Stirling's approximation

$$\begin{aligned} \ln \Omega &= N \ln N - N - \left(\frac{N}{2} - \frac{E}{2\mu H}\right) \ln \left(\frac{N}{2} - \frac{E}{2\mu H}\right) + \left(\frac{N}{2} - \frac{E}{2\mu H}\right) \\ &\quad - \left(\frac{N}{2} + \frac{E}{2\mu H}\right) \ln \left(\frac{N}{2} + \frac{E}{2\mu H}\right) + \left(\frac{N}{2} + \frac{E}{2\mu H}\right) \end{aligned}$$

$$\begin{aligned}
 &= N \ln N - \left(\frac{N}{2} - \frac{E}{2\mu H} \right) \ln \left(\frac{N}{2} - \frac{E}{2\mu H} \right) - \left(\frac{N}{2} + \frac{E}{2\mu H} \right) \ln \left(\frac{N}{2} + \frac{E}{2\mu H} \right) \\
 \therefore \frac{\partial \ln \Omega}{\partial E} &= \frac{1}{2\mu H} \ln \left(\frac{N}{2} - \frac{E}{2\mu H} \right) + \frac{1}{2\mu H} - \frac{1}{2\mu H} \ln \left(\frac{N}{2} + \frac{E}{2\mu H} \right) - \frac{1}{2\mu H} \\
 &= \frac{1}{2\mu H} \ln \left[\frac{\frac{N}{2} - \frac{E}{2\mu H}}{\frac{N}{2} + \frac{E}{2\mu H}} \right] \\
 \frac{1}{kT} &= \frac{1}{2\mu H} \ln \left[\frac{\frac{N}{2} - \frac{E}{2\mu H}}{\frac{N}{2} + \frac{E}{2\mu H}} \right] \\
 \Rightarrow \frac{\frac{N}{2} - \frac{E}{2\mu H}}{\frac{N}{2} + \frac{E}{2\mu H}} &= e^{\frac{2\mu H}{kT}} \\
 \Rightarrow \frac{N}{E} &= \frac{e^{\frac{2\mu H}{kT} + 1}}{e^{\frac{2\mu H}{kT} - 1}} \\
 \Rightarrow -\frac{N\mu H}{E} &= \frac{e^{\frac{\mu H}{kT} + e^{-\frac{\mu H}{kT}}}}{e^{\frac{\mu H}{kT} - e^{-\frac{\mu H}{kT}}}} = \coth \left(\frac{\mu H}{kT} \right) \\
 \therefore E &= -N\mu H \tanh \left(\frac{\mu H}{kT} \right)
 \end{aligned}$$

This is the relation between energy E and temperature T .

PROBLEM 2.2: Consider an extreme relativistic gas, characterized by the single particle energy states $\epsilon(n_x, n_y, n_z) = \frac{hc}{2l} (n_x^2 + n_y^2 + n_z^2)^{\frac{1}{2}}$. Calculate Ω and hence show that the ratio $\gamma = \frac{C_p}{C_v} = \frac{4}{3}$.

SOLUTION

The single particle energy states are given by

$$\epsilon(n_x, n_y, n_z) = \frac{hc}{2l} (n_x^2 + n_y^2 + n_z^2)^{\frac{1}{2}} \quad (\text{i})$$

$$\therefore n_x^2 + n_y^2 + n_z^2 = \frac{4\epsilon^2 L^2}{h^2 c^2} = \frac{4\epsilon^2 V^{\frac{2}{3}}}{h^2 c^2} \quad (\text{ii})$$

Then the total energy of the system is given by

$$E = \sum_r \epsilon_r = \frac{hc}{2L} \sum_{r=1}^N (n_{rx}^2 + n_{ry}^2 + n_{rz}^2)^{\frac{1}{2}} \quad (\text{iii})$$

$$\Rightarrow n_{1x}^2 + n_{1y}^2 + n_{1z}^2 + n_{2x}^2 + n_{2y}^2 + n_{2z}^2 + \dots + n_{N_x}^2 + n_{N_y}^2 + n_{N_z}^2 = \frac{4L^2 E^2}{h^2 c^2} = R^2 \quad (\text{say})$$

This is the equation of a sphere of radius R in $3N$ -dimensional space; the surface of the sphere corresponds to a constant energy E . The number of microstates $\Omega(N, V, E)$ is equal to the number of lattice points on the positive segment of this spherical surface. If the energy of the system is specified in between E and $E + \delta E$, the number of microstates $\Omega(N, V, E \rightarrow E + \delta E)$ within this range is equal to the number of lattice points lying within the positive part of the spherical shell formed between the surfaces of radii R and $R + \delta R$ in the $3N$ -dimensional space.

If $\Phi(N, V, E)$ is the volume of the positive part of the $3N$ -dimensional sphere of radius R , then

$$\Omega(N, V, E \rightarrow E + \delta E) = \Omega = \Phi(N, V, E + \delta E) - \Phi(N, V, E)$$

By Taylor's expansion,

$$\begin{aligned} \Phi(N, V, E + \delta E) &= \Phi(N, V, E) + \frac{\partial \Phi}{\partial E} \delta E + \frac{1}{2!} \frac{\partial^2 \Phi}{\partial E^2} (\delta E)^2 + \dots \\ &\cong \Phi(N, V, E) + \frac{\partial \Phi}{\partial E} \delta E \end{aligned}$$

$$\therefore \Omega = \Phi(N, V, E + \delta E) - \Phi(N, V, E) \cong \frac{\partial \Phi}{\partial E} \delta E \quad (\text{iv})$$

Now from appendix II, the volume of the $3N$ -dimensional sphere of radius R is

$$V_{3N}(R) = \frac{\pi^{\frac{3N}{2}}}{\left(\frac{3N}{2}\right)!} R^{3N} \quad (\text{v})$$

Hence,

$$\Phi(N, V, E) = \left(\frac{1}{2}\right)^{3N} \frac{\pi^{\frac{3N}{2}}}{\left(\frac{3N}{2}\right)!} \left(\frac{2LE}{hc}\right)^{3N} = \frac{\left(\frac{\sqrt{\pi}L}{hc}\right)^{3N} E^{3N}}{\left(\frac{3N}{2}\right)!} \quad (\text{vi})$$

$$\therefore \frac{\partial \Phi}{\partial E} = \frac{3N \left(\frac{\sqrt{\pi}L}{hc}\right)^{3N} E^{3N-1}}{\left(\frac{3N}{2}\right)!} = \frac{3N}{E} \Phi \quad (\text{vii})$$

Thus,

$$\Omega = \frac{\partial \Phi}{\partial E} \delta E = 3N \Phi(N, V, E) \frac{\delta E}{E} \quad (\text{viii})$$

Taking log on both sides

$$\ln \Omega = \ln \Phi + \ln 3N + \ln \frac{\delta E}{E} \quad (\text{ix})$$

But from (vi), we have

$$\ln \Phi = N \ln \left[\frac{\sqrt{\pi}LE}{hc} \right] - \ln \left(\frac{3N}{2} \right)! \cong N \ln \left[\frac{\sqrt{\pi}LE}{hc} \right] - \frac{3N}{2} \ln \left(\frac{3N}{2} \right) + \frac{3N}{2} \quad (\text{x})$$

where we use Stirling's approximation.

$$\begin{aligned} \therefore \ln \Omega &= N \ln \left[\frac{\sqrt{\pi} LE}{hc} \right] - \frac{3N}{2} \ln \left(\frac{3N}{2} \right) + \frac{3N}{2} + \ln 3N + \ln \frac{\delta E}{E} \\ &= \frac{3}{2} N \ln \left[\frac{2}{3N} \left(\frac{\sqrt{\pi} LE}{hc} \right)^{\frac{2}{3}} \right] + \frac{3N}{2} + \ln 3N + \ln \frac{\delta E}{E} \end{aligned}$$

For macroscopic systems, $N \gg 1$ and so $\ln(3N) \ll 3N$. Again since $\delta E \ll E$, $\ln \left(\frac{\delta E}{E} \right)$ is negligible and so

$$\ln \Omega \cong \frac{3}{2} N \ln \left[\frac{2}{3N} \left(\frac{\sqrt{\pi} LE}{hc} \right)^{2/3} \right] + \frac{3N}{2} \quad (\text{xix})$$

Then the entropy of the system is

$$S = k \ln \Omega = \frac{3}{2} Nk \ln \left[\frac{2}{3N} \left(\frac{\sqrt{\pi} LE}{hc} \right)^{2/3} \right] + \frac{3Nk}{2} \quad (\text{xxii})$$

Solving for E ,

$$E = \frac{hc}{\sqrt{\pi} L} \left(\frac{3N}{2} \right)^{\frac{3}{2}} e^{\left(\frac{S}{Nk} \frac{3}{2} \right)} \quad (\text{xxiii})$$

The temperature of the gas is given by

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_{N,V} = \frac{Nk}{E} \Rightarrow E = NkT \quad (\text{xxiv})$$

The specific heat at constant volume is

$$C_V = \left(\frac{\partial E}{\partial T} \right)_{N,S} = Nk \quad (\text{xxv})$$

For the pressure of the system, we obtain

$$P = - \left(\frac{\partial E}{\partial V} \right)_{N,S} = \frac{E}{3V} \quad (\text{xxvi})$$

The specific heat at constant pressure is

$$C_P = \left(\frac{\partial E}{\partial T} \right)_{N,P} + P \left(\frac{\partial V}{\partial T} \right)_{N,P} = \left(\frac{\partial E}{\partial T} \right)_{N,P} + \frac{1}{3} \left(\frac{\partial E}{\partial T} \right)_{N,P} = \frac{4}{3} \left(\frac{\partial E}{\partial T} \right)_{N,P} = \frac{4}{3} Nk \quad (\text{xxvii})$$

$$\therefore \gamma = \frac{C_P}{C_V} = \frac{4}{3} \quad (\text{Proved}) \quad (\text{xxviii})$$

PROBLEM 2.3: The quantity $\Omega(N, V, E)$ is called the microcanonical partition function. Show that $\ln \Omega(N, V, E) = \ln(\Omega_1 + \Omega_2 + \dots) \cong \ln \Omega_{\max}$, where Ω_{\max} is the largest Ω_i in the series.

SOLUTION

Let us assume that there are as many N systems with Ω_i 's comparable to Ω_{\max} , that is, as many such systems as there are particles in any one system. Thus,

$$\Omega \cong N \times \Omega_{\max} \Rightarrow \ln \Omega \cong \ln \Omega_{\max} + \ln N \quad (\text{i})$$

But $\ln N \ll N$.

$$\therefore \ln \Omega(N, V, E) \cong \ln \Omega_{\max} \quad (\text{Proved}) \quad (\text{ii})$$

PROBLEM 2.4: A one-dimensional chain is made up of N identical elements of length l . The angle between successive elements can be either 0° or 180° , but there is no difference in internal energy between these two possibilities. For the sake of counting, one can think of each element as either pointing to the right (+) or to the left (-). Then one has

$$\begin{aligned} N &= n_+ + n_- \\ L &= l(n_+ - n_-) = l(2n_+ - N). \end{aligned}$$

- Use the microcanonical ensemble to find the entropy as a function of N and n_+ , $S(N, n_+)$.
- Find an expression for the tension in the chain as a function of T , N and n_+ , $\mathfrak{S}(T, N, n_+)$.
- Rearrange (b) to give the length as a function of N , T and \mathfrak{S} .

SOLUTION

(a) The number of ways of choosing n_+ elements from a total of N is $\frac{N!}{(N-n_+)!n_+!}$. It follows that

$$\Omega(N, n_+) = \frac{N!}{(N-n_+)!n_+!} \quad (\text{i})$$

The entropy of the system is

$$S(N, n_+) = k \ln \Omega = k [\ln N! - \ln(N-n_+)! - \ln n_+!]$$

Using Stirling's approximation, the above equation becomes

$$\begin{aligned} S(N, n_+) &\cong k [N \ln N - N - (N-n_+) \ln(N-n_+) - n_+ \ln n_+ + n_+] \\ &= k [N \ln N - (N-n_+) \ln(N-n_+) - n_+ \ln n_+] \end{aligned} \quad (\text{ii})$$

(b)

$$\begin{aligned} \frac{\mathfrak{S}}{T} &= - \left(\frac{\partial S}{\partial L} \right)_{N, E} = - \frac{\partial S}{\partial n_+} \frac{\partial n_+}{\partial L} = - \frac{\partial S}{\partial n_+} \times \frac{1}{2l} \\ &= - \frac{k}{2l} \left[\frac{N-n_+}{N-n_+} + \ln(N-n_+) - \frac{n_+}{n_+} - \ln n_+ \right] \\ &= - \frac{k}{2l} \ln \left(\frac{N-n_+}{n_+} \right) \end{aligned}$$

$$\therefore (N, T, n_+) = - \frac{kT}{2l} \ln \left(\frac{N-n_+}{n_+} \right) \quad (\text{iii})$$

(c) From (iii), we have

$$n_+ = N \frac{1}{1 + \exp\left(-\frac{2l\mathfrak{S}}{kT}\right)} \quad (\text{iv})$$

We now use this expression for n_+ to find L :

$$\begin{aligned} L &= l(2n_+ - N) = Nl \left[\frac{2}{1 + \exp\left(-\frac{2l\mathfrak{S}}{kT}\right)} - 1 \right] = Nl \left[\frac{2}{1 + \exp\left(-\frac{2l\mathfrak{S}}{kT}\right)} - \frac{1 + \exp\left(-\frac{2l\mathfrak{S}}{kT}\right)}{1 + \exp\left(-\frac{2l\mathfrak{S}}{kT}\right)} \right] \\ &= Nl \frac{1 - \exp\left(-\frac{2l\mathfrak{S}}{kT}\right)}{1 + \exp\left(-\frac{2l\mathfrak{S}}{kT}\right)} = Nl \frac{\exp\left(-\frac{l\mathfrak{S}}{kT}\right) - \exp\left(-\frac{l\mathfrak{S}}{kT}\right)}{\exp\left(-\frac{l\mathfrak{S}}{kT}\right) + \exp\left(-\frac{l\mathfrak{S}}{kT}\right)} \\ \therefore L &= Nl \tanh\left(\frac{l\mathfrak{S}}{kT}\right) \quad (\text{v}) \end{aligned}$$

For high temperatures, where $kT \gg l\mathfrak{S}$, $\tanh x \rightarrow x$ for x , so

$$L = \frac{Nl^2}{kT} \mathfrak{S} \quad (\text{vi})$$

The fact that the length is proportional to the tension \mathfrak{S} shows that Hooke's law applies to this system, at least for high temperatures.

2.1.3 A two-level system

Consider a system of N (non-interacting and distinguishable) particles. Let the only accessible states for the system be the ground state of zero energy and an excited state of energy ε .

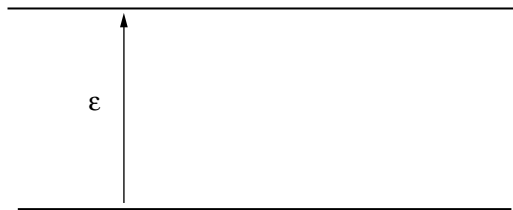


Fig. 2.2. Two non-degenerate energy levels separated by energy.

Let the number of particles in the ground state of zero energy be N_0 and that in the excited state with energy ε be N_ε .

$$\therefore N_0 + N_\varepsilon = N \quad (2.1.25)$$

The total energy of the system is

$$E = (N_0 \times 0) + (N_\varepsilon \times \varepsilon) \Rightarrow N_\varepsilon = \frac{E}{\varepsilon} \quad (2.1.26)$$

If the particles are distinguishable, the number of microstates accessible to the system is equal to the number of ways choosing N_ϵ particles from N particles and is given by

$$\Omega = {}^N C_{N_\epsilon} = \frac{N!}{N_\epsilon! (N - N_\epsilon)!} = \frac{N!}{\frac{E}{\epsilon}! \left(N - \frac{E}{\epsilon}\right)!} \quad (2.1.27)$$

Assuming that N , N_ϵ and $(N - N_\epsilon)$ are all large numbers compared to 1, we use Stirling's approximation for the factorials of large numbers and then the entropy is

$$\begin{aligned} S &= k \ln \Omega = k [N \ln N - N_\epsilon \ln N_\epsilon - (N - N_\epsilon) \ln (N - N_\epsilon)] \\ &= k \left[\left(\frac{E}{\epsilon} - N\right) \ln \left(1 - \frac{E}{N\epsilon}\right) - \frac{E}{\epsilon} \ln \frac{E}{N\epsilon} \right] \end{aligned} \quad (2.1.28)$$

The temperature of the system is given by

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{N,V} = \frac{k}{\epsilon} \ln \left(\frac{N\epsilon}{E} - 1\right) \quad (2.1.29)$$

from which the energy E of the system is given by

$$E = \frac{N\epsilon}{1 + e^{\frac{\epsilon}{kT}}} \quad (2.1.30)$$

$$\therefore N_\epsilon = \frac{E}{\epsilon} = \frac{N}{1 + e^{\frac{\epsilon}{kT}}} \quad (2.1.31)$$

Now for $T \rightarrow 0$, i.e., $\frac{\epsilon}{kT} \gg 1$, $N_\epsilon \rightarrow 0$, that is, all particles are frozen in the ground state. As T increases, both E and N_ϵ increase and when $T \rightarrow \infty$, i.e., $\frac{\epsilon}{kT} \ll 1$, $N_\epsilon \rightarrow \frac{N}{2}$, that is, half the particles are in the ground state and half in the excited state and the energy of the system attains its maximum value of $E \cong \frac{N\epsilon}{2}$. The specific heat at constant volume is given by

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = Nk \left(\frac{\epsilon}{kT}\right)^2 \frac{e^{\frac{\epsilon}{kT}}}{(1 + e^{\frac{\epsilon}{kT}})^2} \quad (2.1.32)$$

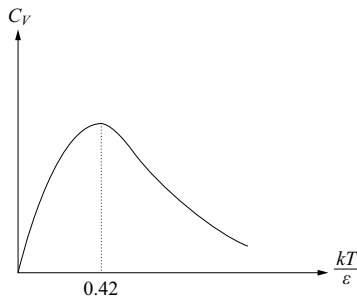


Fig. 2.3. The specific heat at constant volume of a two-state system, showing Schottky hump.

The specific heat C_V is zero at both very low and very high temperatures and is maximum at $T \cong 0.42 \frac{\varepsilon}{k}$. The hump, observed in the C_V vs T plot, is called **Schottky anomaly**. Such a peak, when observed experimentally, is therefore an indication of a gap in its energy states.

2.2 CANONICAL ENSEMBLE

This ensemble is a collection of independent systems having same temperature T , volume V and number N of particles. So the systems of this ensemble are separated by rigid, impermeable, but conducting walls. Since the systems are separated by conducting walls, heat can be exchanged between the systems till they reach a common temperature T . Thus, in canonical ensemble, the systems can exchange energy but not particles.

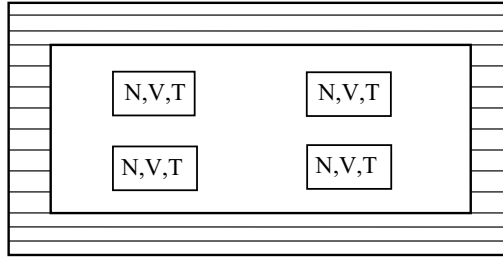


Fig. 2.4. Canonical ensemble.

2.2.1 Probability distribution and canonical partition function

Consider a small system A in thermal interaction with a heat reservoir A' .

What is the probability P_r of finding the system A in any one particular microstate r of energy E_r ?

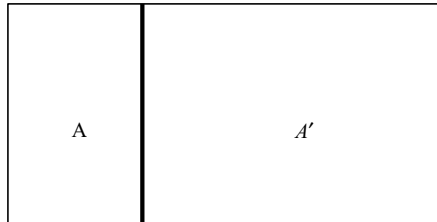


Fig. 2.5. A small system 'A' in thermal interaction with a heat reservoir 'A''.

We assume weak interaction between A and A' , so that their energies are additive. The energy of A is, of course, not fixed. Only the total energy of the combined system, $A^0 = A + A'$ (which is isolated) has a constant value in some range between E^0 and $E^0 + \delta E$:

$$E_r + E' = E^0 = \text{constant} \quad (2.2.1)$$

where E' denotes the energy of the reservoir A' . Thus, when A has an energy E_r , the reservoir A' must have an energy $E' = E^0 - E_r$.

Let $\Omega'(E')$ denote the number of accessible microstates of A' , when it has an energy in the range near E' . If the system A is in the particular state r , the number of states accessible to the combined system A^0 is $1 \times \Omega'(E') = \Omega'(E^0 - E_r)$.

Then the probability of finding the system A in this state is

$$P_r = P_r(E_r) = \frac{\Omega'(E')}{\Omega_{\text{total}}^0} = \frac{\Omega'(E^0 - E_r)}{\Omega_{\text{total}}^0},$$

where Ω_{total}^0 denotes the total number of states accessible to the combined system A^0 .

But $\Omega_{\text{total}}^0 = \text{constant} = c^0$ (say).

$$\therefore P_r = c^0 \Omega'(E^0 - E_r) \quad (2.2.2)$$

$$\Rightarrow \ln P_r = \ln c^0 + \ln \Omega'(E^0 - E_r) \quad (2.2.3)$$

Since A is very small compared to A' , $E_r \ll E^0$. Expanding $\ln \Omega'$ about $E' = E^0$,

$$\ln \Omega'(E^0 - E_r) = \ln \Omega'(E^0) - \left[\frac{\partial \ln \Omega'}{\partial E'} \right]_{E^0} E_r - \dots$$

Since A' acts as a reservoir, $E_r \ll E^0$ and so we can neglect higher order terms.

$$\therefore \ln \Omega'(E^0 - E_r) \cong \ln \Omega'(E^0) - \left[\frac{\partial \ln \Omega'}{\partial E'} \right]_{E^0} E_r \quad (2.2.4)$$

The derivative $\left[\frac{\partial \ln \Omega'}{\partial E'} \right]_{E^0}$ is evaluated at the fixed energy $E' = E^0$ and is thus a constant, independent of the energy E' and $\left[\frac{\partial \ln \Omega'}{\partial E'} \right]_{E^0} = \beta = \frac{1}{kT}$, where T is the temperature of the reservoir.

The equation (2.2.4) then becomes

$$\ln \Omega'(E^0 - E_r) = \ln \Omega'(E^0) - \beta E_r$$

$$\Rightarrow \Omega'(E^0 - E_r) = \Omega'(E^0) e^{-\beta E_r}$$

Since $\Omega'(E^0)$ is just a constant, independent of r , equation (2.2.2) becomes

$$\boxed{P_r = c e^{-\beta E_r}} \quad (2.2.5)$$

where c is a constant, independent of r .

The probability (2.2.5) is a very general result and is of fundamental importance in statistical mechanics. The exponential factor $e^{-\beta E_r}$ is called the '**Boltzmann factor**'; the corresponding probability distribution (2.2.5) is known as the '**canonical distribution**'.

Now according to the normalization conditions for probabilities,

$$\sum_r P_r = 1 \Rightarrow c^{-1} = \sum_r e^{-\beta E_r}$$

$$\therefore \quad \boxed{P_r = \frac{e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} = \frac{e^{-\beta E_r}}{Z}} \quad (2.2.6)$$

where

$$Z = \sum_r e^{-\beta E_r} \quad (2.2.6a)$$

‘ Z ’ is called the **canonical partition function**. (The letter Z is used because the German name is **Zustandsumme**.) It is the sum over all accessible microstates of the system A .

It should be noted that the expression (2.2.6a) is correct, if the energy levels are discrete and non-degenerate. In the general case, an energy level E_r consists of a group of states g_r in number all of the same energy E_r and of equal probability. Thus in summing over all accessible microstates, it is necessary to repeat equal terms (involving E_r) g_r times. Instead, it is simpler to use a modified form of the partition function

$$\boxed{Z = \sum_r g_r e^{-\beta E_r}} \quad (2.2.6b)$$

where the label r goes over all energy levels. If the level is non-degenerate, then $g_r = 1$. Equation (2.2.6b) is the general form of the partition function.

Accordingly,

$$\boxed{P_r = \frac{g_r e^{-\beta E_r}}{\sum_r g_r e^{-\beta E_r}}} \quad (2.2.6c)$$

Once the probability distribution is known, various mean values can be computed. For example, let x be any quantity assuming the value x_r in state r of the system A . Then the mean value of x is

$$\bar{x} = \frac{\sum_r x_r P_r}{\sum_r P_r} = \frac{\sum_r x_r e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} \quad (2.2.7)$$

2.2.2 Energy fluctuations in the canonical ensemble: correspondence with the microcanonical ensemble

According to equation (2.2.7), the mean energy value is

$$\bar{E} = \frac{\sum_r E_r e^{-\beta E_r}}{\sum_r e^{-\beta E_r}} \quad (2.2.8)$$

Now the canonical partition function is

$$Z = \sum_r e^{-\beta E_r} \Rightarrow -\frac{\partial Z}{\partial \beta} = \sum_r E_r e^{-\beta E_r} \quad (2.2.9)$$

Using (2.2.9) in (2.2.8)

$$\bar{E} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{\partial \ln Z}{\partial \beta}. \quad (2.2.10)$$

2.2.3 To calculate the canonical partition function

1. Classical ideal gas

We consider a classical monatomic gas at an absolute temperature T , contained in a volume V . Let us denote the position vector of the i th molecule by \vec{r}_i , its momentum by \vec{p}_i . Then the total energy of the gas is given by

$$E = \sum_{i=1}^N \frac{p_i^2}{2m} + U(\vec{r}_1, \vec{r}_2 \dots \vec{r}_N) \quad (2.2.17)$$

The first term on the right-hand side of the above equation represents the total kinetic energy of all the molecules and the second term represents the potential energy of interaction between the molecules.

The classical canonical partition is given by

$$\begin{aligned} Z &= \int \exp \left[-\beta \left\{ \frac{1}{2m} (p_1^2 + \dots + p_N^2) + U(\vec{r}_1, \dots, \vec{r}_N) \right\} \right] \frac{d^3 r_1 \dots d^3 r_N d^3 p_1 \dots d^3 p_N}{h_0^{3N}} \\ &= \frac{1}{h_0^{3N}} \int e^{-\frac{\beta p_1^2}{2m}} d^3 p_1 \dots \int e^{-\frac{\beta p_N^2}{2m}} d^3 p_N \int e^{-\beta U(\vec{r}_1 \dots \vec{r}_N)} d^3 r_1 \dots d^3 r_N \end{aligned}$$

Since the kinetic energy is a sum of terms, one for each molecule, the corresponding part of the partition function breaks into a product of N integrals, each identical except for the irrelevant variable of integration and equal to $\int_{-\infty}^{\infty} e^{-\frac{\beta p^2}{2m}} d^3 p$.

Since $U(\vec{r}_1, \dots, \vec{r}_N)$ is not in the form of a simple sum of terms for individual molecules, the integration over the coordinates $\vec{r}_1, \dots, \vec{r}_N$ is very difficult to carry out. This is why the treatment of non-ideal gases is complicated (Chapter 7).

For an ideal gas, we can set $U = 0$ and so the integral becomes trivial:

$$\int d^3 r_1 \dots d^3 r_N = V^N \quad (2.2.18)$$

since each integration extends over the volume V of the container.

$$\therefore Z = \xi^N \quad (2.2.19)$$

where

$$\xi = \frac{V}{h_0^3} \int_{-\infty}^{\infty} e^{-\frac{\beta p^2}{2m}} d^3 p \quad (2.2.20)$$

is the partition function for a single particle.

Equation (2.2.19) is the relation between the single particle canonical partition function and that for the whole system, if the particles of the system are identical, non-interacting and distinguishable.

Now

$$\begin{aligned} \int_{-\infty}^{\infty} e^{-\frac{\beta p^2}{2m}} d^3 p &= \int_{-\infty}^{\infty} e^{-\frac{\beta}{2m}(p_x^2 + p_y^2 + p_z^2)} dp_x dp_y dp_z \\ &= \int_{-\infty}^{\infty} e^{-\frac{\beta p_x^2}{2m}} dp_x \int_{-\infty}^{\infty} e^{-\frac{\beta p_y^2}{2m}} dp_y \int_{-\infty}^{\infty} e^{-\frac{\beta p_z^2}{2m}} dp_z = \left[\sqrt{\frac{2\pi m}{\beta}} \right]^3, \end{aligned}$$

where we use the standard integral $\int_{-\infty}^{\infty} e^{-\alpha x^2} dx = \sqrt{\frac{\pi}{\alpha}}$

$$\therefore \xi = \frac{V}{h_0^3} \left(\frac{2\pi m}{\beta} \right)^{\frac{3}{2}} = \frac{V}{h_0^3} (2\pi m k T)^{\frac{3}{2}} \quad (2.2.21)$$

Using (2.2.21) in (2.2.19)

$$Z(N, V, T) = \frac{V^N}{h_0^{3N}} (2\pi m k T)^{\frac{3N}{2}} \quad (2.2.22)$$

This is the canonical partition function of a classical ideal gas.

What is going to happen, if we would use the same formula, i.e., equation (2.2.19) to calculate the partition function for a system of N indistinguishable, identical, non-interacting particles. To illustrate that this is wrong, we consider two indistinguishable particles:

$$\begin{aligned} Z(N=2, V, T) &= \xi^2 = \sum_{r_1} e^{-\beta \epsilon_{r_1}} \times \sum_{r_2} e^{-\beta \epsilon_{r_2}} \\ &= \underbrace{\sum_{r=r_1=r_2} e^{-2\beta \epsilon_r}}_{\text{particles both in the same state}} + \underbrace{\sum_{r_1 \neq r_2} \sum e^{-\beta(\epsilon_{r_1} + \epsilon_{r_2})}}_{\text{particles in different states}} \end{aligned}$$

However, the particles in the second term are counted twice, but since the particles are indistinguishable this does not generate a new state, because

$$e^{-\beta(\epsilon_{r_1} + \epsilon_{r_2})} = e^{-\beta(\epsilon_{r_2} + \epsilon_{r_1})}.$$

Hence, $Z(N=2, V, T) = \xi^2$ counts the particles in different states falsely twice!

We can correct for that by

$$\begin{aligned} Z(N=2, V, T) &= \sum_{r=r_1=r_2} e^{-2\beta \epsilon_r} + \frac{1}{2} \sum_{r_1 \neq r_2} \sum e^{-\beta(\epsilon_{r_1} + \epsilon_{r_2})} \\ &= \sum_{r=r_1=r_2} e^{-2\beta \epsilon_r} + \frac{1}{2!} \sum_{r_1 \neq r_2} \sum e^{-\beta(\epsilon_{r_1} + \epsilon_{r_2})}. \end{aligned}$$

Similarly, for a system of 3 particles

$$\begin{aligned}
 Z(N=3, V, T) &= \sum_{\substack{r=r_1=r_2=r_3 \\ \text{particles in same state}}} e^{-3\beta\epsilon_r} + \dots + \frac{1}{6} \sum_{\substack{r_1 \neq r_2 \neq r_3 \\ \text{all particles in} \\ \text{different states}}} e^{-\beta(\epsilon_{r_1} + \epsilon_{r_2} + \epsilon_{r_3})} \\
 &= \sum_{\substack{r=r_1=r_2=r_3 \\ \text{particles in same state}}} e^{-3\beta\epsilon_r} + \dots + \frac{1}{3!} \sum_{\substack{r_1 \neq r_2 \neq r_3 \\ \text{all particles in} \\ \text{different states}}} e^{-\beta(\epsilon_{r_1} + \epsilon_{r_2} + \epsilon_{r_3})}
 \end{aligned}$$

In general, for a system of N indistinguishable particles,

$$Z(N, V, T) = \sum_{\substack{r=r_1=r_2=r_3=\dots=r_N \\ \text{all particles in} \\ \text{same state}}} e^{-N\beta\epsilon_r} + \dots + \frac{1}{N!} \sum_{\substack{r_1 \neq r_2 \neq r_3 \\ \text{all particles in} \\ \text{different states}}} e^{-\beta(\epsilon_{r_1} + \epsilon_{r_2} + \epsilon_{r_3} + \dots + \epsilon_{r_N})} \quad (2.2.23)$$

We now use semi-classical argument according to which

1. gas particles are identical
2. only very weak or no interaction between the particles exists
3. there are much more available energy levels than particles (classical continuum of quantum mechanics).

Thus, the probability that any single particle state is occupied by more than one particle is very small. This argument greatly simplifies (2.2.23) because only the last term counts.

Thus, for a system of N indistinguishable, identical, non-interacting particles

$$Z(N, V, T) = \frac{\xi^N}{N!} \quad (2.2.23a)$$

2. Classical non-ideal gas

For a non-ideal monatomic gas, the interaction term $U \neq 0$. Therefore, the canonical partition function for a classical non-ideal gas is given by

$$\begin{aligned}
 Z(N, V, T) &= \int \exp \left[-\beta \left\{ \frac{1}{2m} (p_1^2 + \dots + p_N^2) + U(\vec{r}_1, \dots, \vec{r}_N) \right\} \right] \frac{d^3 r_1 \dots d^3 r_N d^3 p_1 \dots d^3 p_N}{h_0^{3N}} \\
 &= \frac{1}{h_0^{3N}} \int e^{-\frac{\beta p_1^2}{2m}} d^3 p_1 \dots \int e^{-\frac{\beta p_N^2}{2m}} d^3 p_N \int e^{-\beta U(\vec{r}_1, \dots, \vec{r}_N)} d^3 r_1 \dots d^3 r_N \\
 \therefore Z(N, V, T) &= \frac{1}{h_0^{3N}} \left(\frac{2\pi m}{\beta} \right)^{\frac{3N}{2}} Q \quad (2.2.24)
 \end{aligned}$$

where

$$Q = \int e^{-\beta U(\vec{r}_1, \dots, \vec{r}_N)} d^3 r_1 \dots d^3 r_N$$

known as configurational partition function (chapter 7). The calculation of Q is quite difficult. For the sake of simplicity, we apply mean field approximation. Then equation (2.2.24) becomes

$$Z(N, V, T) = \frac{1}{h_0^{3N}} \left(\frac{2\pi m}{\beta} \right)^{\frac{3N}{2}} \left[\int_0^V e^{-U_M \beta} d^3 r \right]^N$$

where U_M is the mean field. We take it as follows:

$$U_M = \begin{cases} \infty, & r < r_0 \\ -\bar{U}, & r \geq r_0 \end{cases}$$

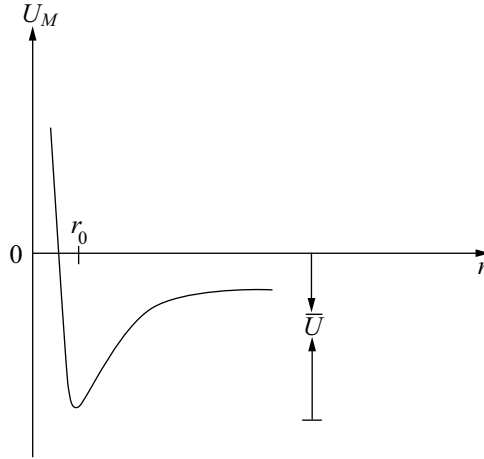


Fig. 2.6. U_M vs. r plot.

Therefore,

$$Z(N, V, T) = \frac{1}{h_0^{3N}} \left(\frac{2\pi m}{\beta} \right)^{\frac{3N}{2}} \left[\int_0^{V_0} e^{-U_M \beta} d^3 r + \int_{V_0}^V e^{-U_M \beta} d^3 r \right]^N \quad (2.2.25)$$

where V_0 is the volume corresponding to $r = r_0$. Now in the range 0 to V_0 , $U_M \rightarrow \infty$ and in the range V_0 to V , $U_M = -\bar{U}$. Therefore, equation (2.2.25) becomes

$$\begin{aligned} Z(N, V, T) &= \frac{1}{h_0^{3N}} \left(\frac{2\pi m}{\beta} \right)^{\frac{3N}{2}} \left[\int_{V_0}^V e^{\bar{U} \beta} d^3 r \right]^N \\ \Rightarrow Z(N, V, T) &= \frac{1}{h_0^{3N}} (2\pi m k T)^{\frac{3N}{2}} \left[(V - V_0) e^{\frac{\bar{U}}{kT}} \right]^N \end{aligned} \quad (2.2.26)$$

This is the canonical partition function for a classical non-ideal gas in the mean field approximation. This topic will be further discussed in Chapter 7.

2.2.4 Thermodynamic quantities in terms of partition function

All the physical quantities can be expressed completely in terms of the partition function Z . Some of them are shown below.

1. Entropy

According to Boltzmann's entropy relation, the entropy S is related to the thermodynamic probability Ω through the relation

$$S = k \ln \Omega \quad (2.2.27)$$

For a classical system, the total number of molecules is

$$N = \sum_i n_i \quad (2.2.28)$$

and

$$\Omega = N! \prod_i \frac{g_i^{n_i}}{n_i!} \quad (2.2.29)$$

Taking logarithm and then using Stirling's approximation

$$\ln \Omega = N \ln N - N + \sum_i (n_i \ln g_i - n_i \ln n_i + n_i) \quad (2.2.30)$$

According to classical statistics, for equilibrium state [see equation (3.1.7)]

$$n_i = g_i e^{-\alpha} e^{-\beta E_i} = g_i A e^{-\beta E_i} \quad (2.2.31)$$

where A is a new constant. Using (2.2.31) in (2.2.30)

$$\begin{aligned} \ln \Omega &= N \ln N - N + \sum_i \left(n_i \ln g_i - n_i \ln g_i A e^{-\beta E_i} + n_i \right) \\ &= N \ln N - N + \sum_i n_i \ln g_i - \sum_i n_i \ln g_i - \ln A \sum_i n_i + \beta \sum_i n_i E_i + \sum_i n_i \\ &= N \ln N - N - N \ln A + \beta E + N \\ &= N \ln N - N \ln A + \beta E \end{aligned}$$

$$\therefore \ln \Omega = N \ln \frac{N}{A} + \beta E \quad (2.2.32)$$

where we put $\sum_i n_i = N =$ total number of particles and $\sum_i n_i E_i = E =$ total energy of the system.

Again using (2.2.28) in (2.2.31)

$$\sum_i n_i = A \sum_i g_i e^{-\beta E_i} \Rightarrow N = AZ \Rightarrow Z = \frac{N}{A} \quad (2.2.33)$$

where $Z = \sum_i g_i e^{-\beta E_i} \rightarrow$ partition function.

After using (2.2.33), equation (2.2.32) becomes

$$\ln \Omega = N \ln Z + \beta E \quad (2.2.34)$$

Finally, using (2.2.34) in (2.2.27), the expression for entropy becomes

$$\begin{aligned} S &= Nk \ln Z + k\beta E \\ &= Nk \ln Z + k \left(\frac{1}{kT} \right) E \end{aligned}$$

$$\therefore S = Nk \ln Z + \frac{E}{T} \quad (2.2.35)$$

Taking logarithms on both sides

$$\ln Z = N \ln V + \frac{3N}{2} \left[\ln \left(\frac{2\pi mk}{h_0^2} \right) + \ln T \right].$$

Differentiating partially with respect to V

$$\frac{\partial \ln Z}{\partial V} = \frac{N}{V} \quad (2.2.49)$$

Using (2.2.49) in (2.2.48)

$$\bar{p}V = NkT \quad (2.2.50)$$

This is equation of state for an ideal gas.

2. Reproduction of van der Waals' equation of state

From equation (2.2.26), the canonical partition function for a non-ideal gas in the mean field approximation is

$$Z(N, V, T) = \frac{1}{h_0^{3N}} (2\pi mkT)^{3N/2} \left[(V - V_0) e^{\frac{\bar{U}}{kT}} \right]^N$$

Taking logarithms on both sides

$$\ln Z = \frac{3N}{2} \ln \left(\frac{2\pi mkT}{h_0^2} \right) + N \ln (V - V_0) + \frac{N\bar{U}}{kT} \quad (2.2.51)$$

Now, $V_0 \propto N \Rightarrow V_0 = bN$, where b is a constant and $\bar{U} \propto \frac{N}{V} \Rightarrow \bar{U} = \frac{aN}{V}$, where a is also a constant.

Then equation (2.2.51) becomes

$$\ln Z = \frac{3N}{2} \ln \left(\frac{2\pi mkT}{h_0^2} \right) + N \ln (V - bN) + \frac{aN^2}{kTV}$$

Differentiating partially with respect to V

$$\frac{\partial \ln Z}{\partial V} = -akT \left(\frac{N}{V} \right)^2 + \frac{N}{V - bN} \quad (2.2.52)$$

Using (2.2.52) in (2.2.48)

$$\bar{p} = -a \left(\frac{N}{V} \right)^2 + \frac{kTN}{V - bN} \Rightarrow \bar{p} = -\frac{a}{\left(\frac{V}{N}\right)^2} + \frac{kT}{\frac{V}{N} - b}$$

$$\Rightarrow \left[\bar{p} + \frac{a}{\left(\frac{V}{N}\right)^2} \right] \left[\frac{V}{N} - b \right] = kT$$

Let $\frac{V}{N} = v$, known as specific volume.

$$\therefore \left(\bar{p} + \frac{a}{v^2} \right) (v - b) = kT \quad (2.2.53)$$

This is the van der Waals equation of state for a real gas.

2.2.6 Generalized equipartition theorem

Let q_i be the generalized co-ordinate. We want to calculate the ensemble average of the quantity $q_i \left(\frac{\partial H}{\partial q_j} \right)$, where H is the Hamiltonian of the system under consideration. Using $d\tau \equiv d^{3N}q d^{3N}p$, we can write in the canonical ensemble

$$\left\langle q_i \frac{\partial H}{\partial q_j} \right\rangle = \frac{\int \left(q_i \frac{\partial H}{\partial q_j} \right) e^{-\beta H} d\tau}{\int e^{-\beta H} d\tau} \quad (2.2.54)$$

Let us now consider the integral in the numerator. Integrating over q_j by parts, it becomes

$$\int \left[-\frac{1}{\beta} q_i e^{-\beta H} \frac{(q_j)_2}{(q_j)_1} + \frac{1}{\beta} \int \left(\frac{\partial q_i}{\partial q_j} \right) e^{-\beta H} dq_j \right] d\tau_{(j)} \quad (2.2.55)$$

where $(q_j)_1$ and $(q_j)_2$ are the extreme values of the coordinate q_j . If q_j is a space coordinate, then its extreme values will correspond to positions of the walls of the container and so the potential energy would be infinite. The infinite potential energy immediately implies that the Hamiltonian H of the system would be infinite. Therefore, the integrated part, i.e., $\left[-\frac{1}{\beta} q_i e^{-\beta H} \frac{(q_j)_2}{(q_j)_1} \right]$ vanishes. The integral part contains the term $(\partial q_i / \partial q_j)$, which is equal to δ_{ij} . Finally, (2.2.55) becomes

$$\frac{1}{\beta} \delta_{ij} \int e^{-\beta H} d\tau \quad (2.2.55a)$$

Substituting this in (2.2.54)

$$\left\langle q_i \frac{\partial H}{\partial q_j} \right\rangle = \delta_{ij} kT \quad (2.2.56)$$

independent of H .

Similarly

$$\left\langle p_i \frac{\partial H}{\partial p_j} \right\rangle = \delta_{ij} kT \quad (2.2.57)$$

which is independent of the form of the Hamiltonian H .

Equations (2.2.55) and (2.2.56) are known as **generalized equipartition theorem**.

This topic will be further discussed in Chapter 3.

2.2.7 Virial theorem

According to the Hamilton's equations of motion,

$$\dot{p}_i = -\frac{\partial H}{\partial q_i} \quad (2.2.58)$$

Using this in (2.2.57)

$$\langle q_i \dot{p}_i \rangle = -kT \quad (2.2.59)$$

Adding over all i from $i = 1$ to $3N$, we obtain

$$\left\langle \sum_{i=1}^{3N} q_i \dot{p}_i \right\rangle = -3NkT \quad (2.2.60)$$

This is known as the **virial theorem**, because $\sum_i q_i \dot{p}_i$ is known as virial in classical mechanics.

PROBLEM 2.5: Find the classical canonical partition function of a one-dimensional linear harmonic oscillator. Also find its average energy $\langle E \rangle$.

SOLUTION

Since this is a one-dimensional case, the classical canonical partition function is

$$Z = \int e^{-\beta E} \frac{dp dx}{h_0}.$$

where E is the total energy of the oscillator and is given by $E = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2$.

$$\therefore Z = \frac{1}{h_0} \left[\int_{-\infty}^{\infty} e^{-\frac{\beta p^2}{2m}} dp \int_{-\infty}^{\infty} e^{-\frac{1}{2}m\omega^2 x^2} dx \right].$$

Using the standard integral $\int_{-\infty}^{\infty} e^{-\alpha x^2} dx = \sqrt{\frac{\pi}{\alpha}}$,

$$Z = \frac{1}{h_0} \left[\sqrt{\frac{2\pi m}{\beta}} \right] \left[\sqrt{\frac{2\pi}{m\beta\omega^2}} \right] = \frac{2\pi}{h_0\beta\omega} = \frac{2\pi kT}{h_0\omega}.$$

This is the canonical partition function.

The average energy of the oscillator is

$$\langle E \rangle = -\frac{\partial \ln Z}{\partial \beta} = \frac{1}{\beta} = kT.$$

PROBLEM 2.6: Find the canonical partition function of a relativistic classical ideal gas with energy-momentum relationship $E = pc$.

SOLUTION

For a classical ideal gas, the canonical partition function is

$$Z = \int e^{-\beta E} \frac{d^{3N}p d^{3N}x}{h_0^{3N}} = \xi^N,$$

where ξ is the single particle partition function and is given by

$$\begin{aligned} \xi &= \int e^{-\beta pc} \frac{d^3p d^3x}{h_0^3} = \frac{V}{h_0^3} \int_0^\infty dp e^{-\beta pc} p^2 \int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\phi = \frac{4\pi V}{h_0^3} \int_0^\infty dp e^{-\beta pc} p^2 \\ &= \frac{4\pi V}{h_0^3} \frac{1}{(\beta c)^3} \int_0^\infty d(\beta pc) e^{-\beta pc} (\beta pc)^2 = \frac{4\pi V}{h_0^3} \left(\frac{kT}{c} \right)^3 \Gamma(3) \end{aligned}$$

Also ‘ Z ’ can be written as

$$Z = \sum_n^N C_n e^{-\beta n w} \quad (\text{iii})$$

Now the mean value of n is

$$\begin{aligned} \bar{n} &= \frac{\sum_n n^N C_n e^{-\beta n w}}{\sum_n^N C_n e^{-\beta n w}} = \frac{\sum_n n^N C_n e^{-\beta n w}}{Z} = -\frac{1}{w} \frac{\partial \ln Z}{\partial \beta} = -\frac{N}{w} \frac{\partial}{\partial \beta} \left[\ln \left(1 + e^{-\beta w} \right) \right] \\ &= N \frac{e^{-\beta w}}{1 + e^{-\beta w}} \end{aligned}$$

$$\Rightarrow \bar{n} + \bar{n} e^{-\beta w} = N e^{-\beta w} \Rightarrow \frac{\bar{n}}{N - \bar{n}} = e^{\frac{-w}{kT}}$$

When $\bar{n} \ll N$,

$$\bar{n} \approx N e^{\frac{-w}{kT}} \quad (\text{iv})$$

PROBLEM 2.10: Show that the partition function of an extreme relativistic gas consisting of $3N$ indistinguishable particles, with energy-momentum relationship $\varepsilon = pc$, c being the speed of light and moving in one dimension is given by $Z(N, L, T) = \frac{1}{(3N)!} \left[2L \left(\frac{kT}{hc} \right) \right]^{3N}$, where L being the ‘length’ of the space available.

SOLUTION

The single particle canonical partition function is

$$\xi = \frac{1}{h} \int e^{-\beta \varepsilon} dq dp = \frac{L}{h} \int_0^\infty e^{-\beta pc} dp = L \left(\frac{kT}{hc} \right) \quad (\text{i})$$

Therefore, the canonical partition function of the system of N non-interacting **indistinguishable** particles is

$$Z(N, L, T) = \frac{\xi^{3N}}{(3N)!} = \frac{1}{(3N)!} \left[L \left(\frac{kT}{hc} \right) \right]^{3N} \quad (\text{ii})$$

PROBLEM 2.11: Consider a system in thermal equilibrium at temperature T – its two states with energy difference 4.8×10^{-14} erg occur with relative probability e^2 erg / deg. Calculate the temperature. Boltzmann’s constant $k = 1.38 \times 10^{-16}$ erg / deg.

SOLUTION

Let P_1 and P_2 be respectively the probabilities of the state of energies E_1 and E_2 . Then $P_1 = c e^{-\frac{E_1}{kT}}$ and $P_2 = c e^{-\frac{E_2}{kT}}$, where c is a constant of proportionality.

$$\therefore \frac{P_1}{P_2} = e^{\frac{(E_2 - E_1)}{kT}} \Rightarrow T = \frac{(E_2 - E_1)}{k \ln \left(\frac{P_1}{P_2} \right)} = \frac{4.8 \times 10^{-14}}{1.38 \times 10^{-16} \times \ln e^2} = 173.913 \text{ K}$$

PROBLEM 2.12: The first vibrational energy of a diatomic molecule is 600 cm^{-1} above the ground state. Calculate the relative population of molecules in these two levels at $T = 400 \text{ K}$.

SOLUTION

Let N_0 and E_0 be respectively the number of molecules and the energy of the ground state and N_1 and E_1 be the corresponding values for the first excited state.

$$\therefore N_1 = N_0 e^{-\frac{(E_1 - E_0)}{kT}} \quad (\text{i})$$

Now

$$(E_1 - E_0) = h\nu = \frac{h\lambda}{c} = hc\bar{\nu} = 6.6 \times 10^{-27} \times 3 \times 10^{10} \times 600 = 1.2 \times 10^{-13} \text{ erg}$$

$$\therefore \frac{N_1}{N_0} = e^{-\frac{(E_1 - E_0)}{kT}} = e^{-\left(\frac{1.2 \times 10^{-13}}{1.38 \times 10^{-16} \times 400}\right)} \cong 0.1 \Rightarrow N_1 = 0.1 \times N_0$$

PROBLEM 2.13: Consider a system which can take only three different energy states $E_1 = 0$, $E_2 = 1.38 \times 10^{-14}$ ergs, $E_3 = 2.76 \times 10^{-14}$ ergs. Find the probability that at temperature 100 K the system may be (a) in one of the microstates of energy E_3 , (b) in the ground state E_1 .

SOLUTION

Let P_1 , P_2 and P_3 be respectively the probabilities with which the microstates can occur in three energy values E_1 , E_2 and E_3 .

$$\text{Then } P_1 = ce^{-\frac{E_1}{kT}} = c$$

$$P_2 = ce^{-\frac{E_2}{kT}} = ce^{-\frac{1.38 \times 10^{-14}}{1.38 \times 10^{-16} \times 100}} = ce^{-1}$$

and

$$P_3 = ce^{-\frac{E_3}{kT}} = ce^{-\frac{2.76 \times 10^{-14}}{1.38 \times 10^{-16} \times 100}} = ce^{-2}$$

where c is a constant of proportionality.

Again these three states can occur in 2, 5 and 4 different ways respectively. Then $P_1 = 2c$, $P_2 = 5ce^{-1}$ and $P_3 = 4ce^{-2}$. But

$$\sum_{i=1}^3 P_i = 1 \Rightarrow (P_1 + P_2 + P_3) = 1 \Rightarrow (2c + 5ce^{-1} + 4ce^{-2}) = 1$$

$$\Rightarrow c = \frac{1}{2 + 1.84 + 0.54} \Rightarrow c = \frac{1}{4.38}$$

Since $e = 2.72$.

(a) The probability for the system to be in one of the microstates of energy E_3 is

$$P_3 = 4ce^{-2} = \frac{4}{4.38 \times (2.72)^2} = 0.12.$$

Again

$$\bar{E} = -\frac{\partial \ln Z}{\partial \beta} \quad (\text{vi})$$

Comparing (v) and (vi)

$$\begin{aligned} F\beta &= -\ln Z \\ \Rightarrow F &= -kT \ln Z \end{aligned} \quad (\text{vii})$$

Finally, using (vii) in (iii)

$$\begin{aligned} \sum_r P_r \ln P_r &= -\frac{\bar{E}}{kT} + \frac{F}{kT} = \frac{1}{kT}(F - \bar{E}) = \frac{1}{kT}(-TS) = -\frac{S}{k} \\ \Rightarrow S &= -k \sum_r P_r \ln P_r \quad [\text{Proved}] \end{aligned} \quad (\text{viii})$$

In case of microcanonical ensemble, we have a group of Ω states (which are equally likely to occur) for each member. The value of P_r is then $\frac{1}{\Omega}$ for each of these states and 0 for all others. Consequently,

$$S = -k \sum_{r=1}^{\Omega} \left\{ \frac{1}{\Omega} \ln \left(\frac{1}{\Omega} \right) \right\} = k \ln \Omega \quad [\text{Proved}] \quad (\text{ix})$$

PROBLEM 2.17: The states of a system are (i) a group of g_1 equally likely states with a common energy ε_1 , and (ii) a group of g_2 equally likely states with a common energy $\varepsilon_2 \neq \varepsilon_1$.

- (a) Show that the entropy of the system is given by $S = -k \left[P_1 \ln \left(\frac{P_1}{g_1} \right) + P_2 \ln \left(\frac{P_2}{g_2} \right) \right]$
- (b) Also show that $S = k \left[\ln g_1 + \ln \left\{ 1 + \left(\frac{g_2}{g_1} \right) e^{-x} \right\} + \frac{x}{1 + (g_1/g_2)e^x} \right]$, where $x = \frac{\varepsilon_2 - \varepsilon_1}{kT}$, assumed positive.
- (c) Check that at $T \rightarrow 0, S \rightarrow k \ln g_1$.

SOLUTION

(a) The canonical partition function is

$$Z = \sum_r g_r e^{-\beta E_r} \quad (\text{i})$$

and

$$P_r = \frac{g_r e^{-\beta E_r}}{Z} \quad (\text{ii})$$

$$\therefore \frac{P_r}{g_r} = \frac{e^{-\beta E_r}}{Z} \Rightarrow \ln \left(\frac{P_r}{g_r} \right) = -\ln Z - \beta E_r$$

$$\Rightarrow \sum_r P_r \ln \left(\frac{P_r}{g_r} \right) = -\ln Z - \beta \bar{E} \quad (\text{iii})$$

The Helmholtz free energy is

$$F = \bar{E} - TS$$

$$\Rightarrow dF = d\bar{E} - TdS - SdT = d\bar{E} - (d\bar{E} + PdV) - SdT = -PdV - SdT$$

$$\therefore \left. \begin{aligned} S &= - \left(\frac{\partial F}{\partial T} \right)_V \\ P &= - \left(\frac{\partial F}{\partial V} \right)_T \end{aligned} \right\} \quad (\text{iv})$$

Hence,

$$\bar{E} = F + TS = F - T \left(\frac{\partial F}{\partial T} \right)_V = F + \beta \left(\frac{\partial F}{\partial \beta} \right)_V = \left[\frac{\partial}{\partial \beta} (F\beta) \right]_V \quad (\text{v})$$

Again

$$\bar{E} = - \frac{\partial \ln Z}{\partial \beta} \quad (\text{vi})$$

Comparing (v) and (vi)

$$F = -kT \ln Z \quad (\text{vii})$$

Using (vii) in (iii), we obtain

$$\sum_r P_r \ln \left(\frac{P_r}{g_r} \right) = \frac{F - \bar{E}}{kT} = -\frac{S}{k} \Rightarrow S = -k \sum_r P_r \ln \left(\frac{P_r}{g_r} \right)$$

$$\therefore S = -k \left[P_1 \ln \left(\frac{P_1}{g_1} \right) + P_2 \ln \left(\frac{P_2}{g_2} \right) \right] \quad (\text{Proved}) \quad (\text{viii})$$

(b) We know that

$$\left. \begin{aligned} P_1 &= \frac{g_1 e^{-\beta \epsilon_1}}{Z} \\ P_2 &= \frac{g_2 e^{-\beta \epsilon_2}}{Z} \end{aligned} \right\} \quad (\text{ix})$$

Using (ix) in (viii)

$$\begin{aligned} S &= -k [P_1(-\beta \epsilon_1 - \ln Z) + P_2(-\beta \epsilon_2 - \ln Z)] \\ &= k [\beta (P_1 \epsilon_1 + P_2 \epsilon_2) + (P_1 + P_2) \ln Z] \\ &= k [\beta (P_1 \epsilon_1 + P_2 \epsilon_2) + \ln Z] \quad (\because P_1 + P_2 = 1) \\ &= k \left[\beta \left(\frac{g_1 \epsilon_1 e^{-\beta \epsilon_1} + g_2 \epsilon_2 e^{-\beta \epsilon_2}}{Z} \right) + \ln Z \right] \\ &= k \left[\beta \left(\frac{g_1 \epsilon_1 e^{-\beta \epsilon_1} + g_2 \epsilon_2 e^{-\beta \epsilon_2}}{g_1 e^{-\beta \epsilon_1} + g_2 e^{-\beta \epsilon_2}} \right) + \ln (g_1 e^{-\beta \epsilon_1} + g_2 e^{-\beta \epsilon_2}) \right] \\ &= k \left[\beta \left(\frac{g_1 \epsilon_1 e^{-\beta \epsilon_1} + g_2 \epsilon_2 e^{-\beta \epsilon_2}}{g_1 e^{-\beta \epsilon_1} + g_2 e^{-\beta \epsilon_2}} \right) + \ln (g_1 e^{-\beta \epsilon_1}) + \ln \left\{ 1 + \frac{g_2}{g_1} e^{-\beta (\epsilon_2 - \epsilon_1)} \right\} \right] \end{aligned}$$

If the temperature T is so high that the thermal energy kT is large compared to the separation $h\nu$ between energy levels, i.e., $\beta h\nu = \frac{h\nu}{kT} \ll 1$,

$$\langle E \rangle \approx h\nu \left(\frac{1}{2} + \frac{1}{\frac{h\nu}{kT}} \right) = h\nu \left(\frac{1}{2} + \frac{kT}{h\nu} \right) \approx h\nu \times \frac{kT}{h\nu} = kT \longrightarrow \text{classical result.}$$

PROBLEM 2.19: A classical point particle is moving in a 3-dimensional harmonic oscillator potential well, $V(r) = 1/2Kr^2 = 1/2K(x^2 + y^2 + z^2)$ at absolute temperature T . Obtain a formula for the probability that the particle is in between r and $r + dr$ from the centre of attraction. Also obtain a formula for the mean square distance of the particle from the centre of attraction and check your result by comparison with the equipartition principle.

SOLUTION

The probability that the particle will be in phase space volume element d^3rd^3p

$$= \frac{e^{-\frac{\beta p^2}{2m} - \beta \frac{1}{2}Kr^2} d^3pd^3r}{\int e^{-\frac{\beta p^2}{2m} - \beta \frac{1}{2}Kr^2} d^3pd^3r} = \frac{e^{-\frac{\beta p^2}{2m} - \beta \frac{1}{2}Kr^2} d^3pr^2 \sin\theta d\theta d\phi dr}{\int e^{-\frac{\beta p^2}{2m} - \beta \frac{1}{2}Kr^2} d^3pr^2 \sin\theta d\theta d\phi dr}$$

Therefore, the probability that the particle will lie in the range r and $r + dr$ is

$$P(r)dr = \frac{\int \int \int e^{-\frac{\beta Kr^2}{2}} r^2 \sin\theta d\theta d\phi dr e^{-\frac{\beta p^2}{2m}} d^3p}{\int \int \int \int e^{-\frac{\beta Kr^2}{2}} r^2 \sin\theta d\theta d\phi dr e^{-\frac{\beta p^2}{2m}} d^3p}$$

$$= \frac{e^{-\frac{\beta Kr^2}{2}} r^2 dr}{\int_0^\infty e^{-\frac{\beta Kr^2}{2}} r^2 dr} = \frac{e^{-\frac{\beta Kr^2}{2}} r^2 dr}{\frac{1}{4}\sqrt{\pi} \left(\frac{2}{K\beta} \right)^{\frac{3}{2}}}$$

$$\therefore P(r)dr = \frac{4}{\sqrt{\pi}} \left(\frac{K\beta}{2} \right)^{\frac{3}{2}} e^{-\frac{1}{2}\beta Kr^2} r^2 dr \quad (\text{i})$$

The mean square distance is

$$\langle r^2 \rangle = \frac{\int r^2 P(r) dr}{\int P(r) dr} = \frac{\int_0^\infty r^4 e^{-\frac{\beta Kr^2}{2}} dr}{\int_0^\infty r^2 e^{-\frac{\beta Kr^2}{2}} dr} = \frac{\frac{3}{8}\sqrt{\pi} \left(\frac{2}{\beta K} \right)^{\frac{5}{2}}}{\frac{1}{4}\sqrt{\pi} \left(\frac{2}{\beta K} \right)^{\frac{3}{2}}} = \frac{3}{2} \left(\frac{2}{\beta K} \right) = \frac{3kT}{K} \quad (\text{ii})$$

Therefore, the average potential energy $= \frac{1}{2}K\langle r^2 \rangle = \frac{1}{2}K \frac{3kT}{K} = \frac{3}{2}kT$, which is consistent with the equipartition law.

PROBLEM 2.20: Suppose a system of N non-interacting particles at temperature T in an external magnetic field \vec{H} pointing along the z-direction. Assume that each atom has spin 1/2 and an intrinsic magnetic moment $\vec{\mu}$.

1. If the magnetic moment of each atom can point either parallel or anti-parallel to the external field \vec{H} , what is the mean magnetic moment $\langle \mu_H \rangle$ (in the direction of \vec{H} , i.e., z-direction) of such atom ?
2. Calculate the partition function of one atom, the mean magnetic moment along the field direction and hence the susceptibility of the system, first by treating the system classically and then quantum mechanically.

SOLUTION

Each atom can be in two possible states: the state (+) where its spin points up (i.e., parallel to \vec{H}) and the state (-) where its spin points down (i.e. anti-parallel to \vec{H}). In the (+) state, $\vec{\mu}$ is parallel to \vec{H} and so $\mu_H = \mu$. The corresponding magnetic energy of the atom is $E_+ = -\mu H$. The probability of finding the atom in this state is

$$P_+ = C e^{-\beta E_+} = C e^{\beta \mu H} \quad (\text{i})$$

where C is a constant of proportionality and $\beta = \frac{1}{kT}$. Similarly, in the (-) state, $\vec{\mu}$ is anti-parallel to \vec{H} and so $\mu_H = -\mu$. The corresponding magnetic energy of the atom is $E_- = +\mu H$. The probability of finding the atom in this state is

$$P_- = C e^{-\beta E_-} = C e^{-\beta \mu H} \quad (\text{ii})$$

\therefore The mean value of μ_H is

$$\langle \mu_H \rangle = \frac{P_+(\mu) + P_-(-\mu)}{P_+ + P_-} = \mu \frac{e^{\beta \mu H} - e^{-\beta \mu H}}{e^{\beta \mu H} + e^{-\beta \mu H}} = \mu \tanh(\beta \mu H) = \mu \tanh\left(\frac{\mu H}{kT}\right).$$

When the system is treated classically

The energy of a magnetic dipole in the presence of the external magnetic field is

$$E = -\vec{\mu} \cdot \vec{H} = -\mu H \cos \theta \quad (\text{iii})$$

The canonical partition function of the system is

$$Z = \xi^N \quad (\text{iv})$$

where ξ is the single particle canonical partition function and is given by

$$\xi = \sum_{\theta} \exp(\beta \mu H \cos \theta) = \int_{\phi=0}^{2\pi} \int_{\theta=0}^{\pi} e^{\beta \mu H \cos \theta} \sin \theta \, d\theta \, d\phi = 4\pi \frac{\sinh(\beta \mu H)}{\beta \mu H} \quad (\text{v})$$

$$\therefore Z = \left[4\pi \frac{\sinh(\beta \mu H)}{\beta \mu H} \right]^N \quad (\text{vi})$$

The average magnetic moment along the field direction is given by

$$\begin{aligned} \mu_H = \langle \mu \cos \theta \rangle &= \frac{\sum_{\theta} \mu \cos \theta \exp(\beta \mu H \cos \theta)}{\sum_{\theta} \exp(\beta \mu H \cos \theta)} = \frac{1}{\beta} \frac{\partial}{\partial H} \ln \xi = \mu \left[\coth(\beta \mu H) - \frac{1}{\beta \mu H} \right] \\ &= \mu L(\beta \mu H) \end{aligned} \quad (\text{vii})$$

where $L(x)$ is the so-called **Langevin function**:

$$L(x) = \coth x - \frac{1}{x} \quad (\text{viii})$$

Therefore, the magnetization of the system is given by

$$M = N\mu_H = N\mu L(x) \quad (\text{ix})$$

For magnetic fields so strong (or temperatures so low) that the parameter $x \gg 1$, $L(x) \cong 1$ and so $M \cong N\mu \rightarrow$ saturation. On the other hand, for high temperatures (or the magnetic fields so weak) that the parameter $x \ll 1$, $L(x) \cong \frac{x}{3}$ and so

$$M \cong \frac{N\mu^2}{3kT}H \quad (\text{x})$$

Therefore, the high temperature susceptibility of the system is given by

$$\chi(T) = \lim_{H \rightarrow 0} \left(\frac{\partial M}{\partial H} \right) = \frac{N\mu^2}{3kT} = \frac{C}{T} \quad (\text{xi})$$

This is **Curie law** of paramagnetism, the constant C being the Curie constant of the system.

When the system is treated quantum mechanically

In this case, the major modification arises from the fact that the magnetic dipole moment $\vec{\mu}$ and its component μ_H along the field direction cannot have arbitrary values.

The magnetic moment $\vec{\mu}$ is related to the total angular momentum $\hbar\vec{J}$ through the relation

$$\vec{\mu} = g\mu_B\vec{J} \quad (\text{xii})$$

where $\mu_B = \frac{e\hbar}{2mc}$, known as Bohr magneton and g is the so-called g factor of the atom, $e =$ charge of an electron, $m =$ mass of an electron and $c =$ velocity of light in vacuum.

Using (xii) in (iii), we have

$$E = -g\mu_B\vec{J} \cdot \vec{H} = -g\mu_B H J_z \quad (\text{xiii})$$

since \vec{H} is along the z -direction. In quantum mechanical description, the values which J_z can assume are discrete and are given by $J_z = m$, where $m = -J, -(J-1), \dots, (J-1), J$.

\therefore The possible energies of the atom are

$$E_m = -g\mu_B H m \quad (\text{xiv})$$

Then the partition function of one atom is

$$Z = \sum_m e^{-\beta E_m} = \sum_{m=-J}^J e^{\beta g\mu_B H m} \quad (\text{xv})$$

Let $x = \beta g \mu_B H = \frac{g \mu_B H}{kT} \rightarrow$ a dimensionless parameter. Therefore,

$$\begin{aligned} Z &= \sum_{m=-J}^J e^{xm} \\ &= \left[e^{-xJ} + e^{-x(J-1)} + \dots + e^{xJ} \right] \\ &= \frac{e^{-xJ} - e^{x(J+1)}}{1 - e^x} = \frac{e^{-x(J+\frac{1}{2})} - e^{x(J+\frac{1}{2})}}{e^{-\frac{x}{2}} - e^{\frac{x}{2}}} = \frac{\sinh\left(J + \frac{1}{2}\right)x}{\sinh\frac{x}{2}} \end{aligned}$$

$$\therefore Z = \frac{\sinh\left(J + \frac{1}{2}\right) \beta g \mu_B H}{\sinh\frac{1}{2} \beta g \mu_B H} \quad (\text{xvi})$$

Now the probability of finding the atom in a state labelled m is given by

$$P_m = C e^{-\beta E_m} \quad (\text{xvii})$$

where C is a constant of proportionality, determined from the normalization condition, $\sum_m P_m = 1$.

Therefore, the mean value of the magnetic moment along the field direction (i.e. z-direction) is

$$\langle \mu_H \rangle = \frac{\sum_m \mu_H P_m}{\sum_m P_m} = \frac{\sum_{m=-J}^J \mu_H e^{\beta g \mu_B H m}}{\sum_{m=-J}^J e^{\beta g \mu_B H m}} \quad (\text{xviii})$$

Since the field \vec{H} is along the z-direction, $\mu_H = \mu_z = g \mu_B J_z = g \mu_B m$, from (iv).

$$\begin{aligned} \therefore \langle \mu_H \rangle &= \frac{\sum_{m=-J}^J g \mu_B m e^{\beta g \mu_B H m}}{\sum_{m=-J}^J e^{\beta g \mu_B H m}} = \frac{1}{\beta} \frac{\sum_{m=-J}^J (\beta g \mu_B m) e^{\beta g \mu_B H m}}{\sum_{m=-J}^J e^{\beta g \mu_B H m}} = \frac{1}{\beta} \frac{1}{Z} \frac{\partial Z}{\partial H} = \frac{1}{\beta} \frac{\partial \ln Z}{\partial H} \\ &= \frac{1}{\beta} \frac{\partial \ln Z}{\partial x} \frac{\partial x}{\partial H} = g \mu_B \frac{\partial \ln Z}{\partial x} = g \mu_B \frac{\partial}{\partial x} \left[\ln \sinh\left(J + \frac{1}{2}\right)x - \ln \sinh\frac{x}{2} \right] \\ &= g \mu_B \left[\frac{\left(J + \frac{1}{2}\right) \cosh\left(J + \frac{1}{2}\right)x}{\sinh\left(J + \frac{1}{2}\right)x} - \frac{\frac{1}{2} \cosh\frac{x}{2}}{\sinh\frac{x}{2}} \right] \end{aligned}$$

$$\Rightarrow \langle \mu_H \rangle = g \mu_B J B_J(x)$$

where $B_J(x) = \frac{1}{J} \left[\left(J + \frac{1}{2}\right) \coth\left(J + \frac{1}{2}\right)x - \frac{1}{2} \coth\frac{x}{2} \right]$, known as **Brillouin function**. Therefore, the magnetization of the system is given by

$$M = N \langle \mu_H \rangle = N g \mu_B J B_J(x) \quad (\text{xix})$$

For strong fields and low temperatures ($x \gg 1$), the function $B_J(x) \cong 1$ for all J and so $M \cong N g \mu_B J \rightarrow$ magnetic saturation.

On the other hand, for high temperatures and weak fields ($x \ll 1$), $B_J(x) \cong \frac{1}{3} \left(1 + \frac{1}{J}\right)x$, so that

$$M \cong N \frac{(g\mu_B J)^2}{3kT} \left(1 + \frac{1}{J}\right) H = N \frac{g^2 \mu_B^2 J(J+1)}{3kT} H \quad (\text{xx})$$

Therefore, the susceptibility is given by

$$\chi(T) = \frac{Ng^2 \mu_B^2 J(J+1)}{3kT} \propto \frac{1}{T}, \text{ which shows that the Curie law is again valid.}$$

PROBLEM 2.21: Show that entropy increases when two ideal gases at the same temperature and pressure diffuse into each other. Discuss Gibbs paradox in this connection.

SOLUTION

According to Boltzmann's relation, the entropy S of a system is related to the thermodynamic probability Ω and is given by

$$S = k \ln \Omega \quad (\text{i})$$

From Maxwell-Boltzmann statistical count

$$\begin{aligned} \Omega &= N! \prod_i \frac{g_i^{n_i}}{n_i!} \\ \Rightarrow \ln \Omega &= \ln N! + \sum_i (n_i \ln g_i - \ln n_i!) \\ &= \ln N! + \sum_i (n_i \ln g_i - n_i \ln n_i + n_i) \\ &= \ln N! + \sum_i n_i (\ln g_i - \ln n_i + 1) \\ \Omega &= \ln N! + \sum_i n_i \left(\ln \frac{g_i}{n_i} + 1 \right) \quad (\text{ii}) \end{aligned}$$

Again for most probable state, Ω or $\ln \Omega$ is maximum and then we have

$$n_i = e^{-\alpha} g_i e^{-\frac{E_i}{kT}} \quad (\text{iii})$$

[see equation (3.1.7)].

$$\therefore \frac{n_i}{g_i} = e^{-\left(\alpha + \frac{E_i}{kT}\right)} \Rightarrow \ln \frac{g_i}{n_i} = \alpha + \frac{E_i}{kT} \quad (\text{iv})$$

Using (iv) in (ii)

$$\begin{aligned} \ln \Omega &= \ln N! + \sum_i n_i \left(\frac{E_i}{kT} + \alpha + 1 \right) \\ &= \ln N! + \frac{1}{kT} \sum_i n_i E_i + \alpha \sum_i n_i + \sum_i n_i \end{aligned}$$

$$S_B = \frac{3}{2}Nk + Nk \ln \left[V \left(\frac{2\pi mkT}{h_0^2} \right)^{\frac{3}{2}} \right].$$

Hence, the total entropy is simply

$$S_A + S_B = 3Nk + 2Nk \ln \left[V \left(\frac{2\pi mkT}{h_0^2} \right)^{\frac{3}{2}} \right] \quad (\text{ix})$$

We now remove the partition very slowly so that the gases diffuse into each other. Therefore, the total number of molecules $2N$ of the two gases occupy a volume $2V$. Since there is no change in pressure and temperature, the entropy of the system after the partition is removed is

$$S = 3Nk + 2Nk \ln \left[(2V) \left(\frac{2\pi mkT}{h_0^2} \right)^{\frac{3}{2}} \right] \quad (\text{x})$$

Now, according to the additive property of entropy

$$S = S_A + S_B \quad (\text{xi})$$

But from (ix) and (x), we see that

$$S - [S_A + S_B] = 2Nk \ln 2 > 0. \quad (\text{xii})$$

which is not equal to zero as required by (xi).

This paradox was first discussed by Gibbs and is commonly referred to as the ‘**Gibbs paradox**’.

The root of the difficulty embodied in the Gibbs paradox is that we treated the gas molecules as distinguishable, as though interchanging the positions of two molecules would lead to a physically distinct state of the gas. This is not so. Indeed, if we treated the gas by quantum mechanics, the molecules would have to be regarded as indistinguishable (see Chapter 3). In this case, $N!$ permutations of the molecules among themselves do not lead to physically distinct situations, so that we should subtract the term $k \ln N!$ from (vi), so that

$$S = \frac{5}{2}Nk + Nk \ln \left[\frac{V}{N} \left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} \right] \quad (\text{xiii})$$

This has been verified experimentally at high temperatures and is known as **Sackur-Tetrode equation**.

Equation (xii) can be written as

$$S = Nk \ln \left[\frac{V}{N} \left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} e^{\frac{5}{2}} \right] \quad (\text{xiv})$$

Using this expression, it can be easily verified that $S_A + S_B - S = 0$ and hence the paradox is removed.

PROBLEM 2.22: Imagine that a system R_1 has probability P_r^1 of being found in a state of r and a system R_2 has probability P_s^2 of being found in a state s . Then one has $S_1 = -k \sum_r P_r^1 \ln P_r^1$ and

$S_2 = -k \sum_r P_r^2 \ln P_r^2$. Each state of the composite system $R (= R_1 + R_2)$ can be labelled by a pair of numbers r, s . Let the probability of R being found in this state be denoted by P_{rs} . Then the entropy is defined by $S = -k \sum_r \sum_s P_{rs} \ln P_{rs}$. If R_1 and R_2 are weakly interacting so that they are statistically independent, then $P_{rs} = P_r^1 P_s^2$. Show that under these circumstances, the entropy is simply additive, i.e., $S = S_1 + S_2$.

SOLUTION

We have

$$\begin{aligned}
 S &= -k \sum_r \sum_s P_{rs} \ln P_{rs} = -k \sum_r \sum_s P_r^1 P_s^2 \ln (P_r^1 P_s^2) \quad (\because P_{rs} = P_r^1 P_s^2) \\
 &= \left(\sum_s P_s^2 \right) \left(-k \sum_r P_r^1 \ln P_r^1 \right) + \left(\sum_r P_r^1 \right) \left(-k \sum_s P_s^2 \ln P_s^2 \right) \\
 &= -k \sum_r P_r^1 \ln P_r^1 + \left(-k \sum_s P_s^2 \ln P_s^2 \right) \quad \left(\because \sum_r P_r^1 = 1 = \sum_s P_s^2 \right)
 \end{aligned}$$

$$\therefore S = S_1 + S_2 \quad (\text{Proved})$$

PROBLEM 2.23: Suppose that a system R_1 has probability P_r^1 of being found in a state r and a system R_2 has probability P_s^2 of being found in a state s . The entropy of R_1 is $S_1 = -k \sum_r P_r^1 \ln P_r^1$ and that of R_2 is $S_2 = -k \sum_s P_s^2 \ln P_s^2$. Each state of the composite system $R (= R_1 + R_2)$ is then labelled by the pair numbers r, s . Let the probability of R being found in this state be P_{rs} ; its entropy is defined by $S = -k \sum_r \sum_s P_{rs} \ln P_{rs}$. Assume that R_1 and R_2 are not weakly interacting, so that $P_{rs} \neq P_r^1 P_s^2$. Of course $P_r^1 = \sum_s P_{rs}$ and $P_s^2 = \sum_r P_{rs}$. Moreover, all the probabilities are properly normalized so that $\sum_r P_r^1 = 1$, $\sum_s P_s^2 = 1$, $\sum_r \sum_s P_{rs} = 1$. Show that

$$\text{(a)} \quad S - (S_1 + S_2) = k \sum_{r,s} P_{rs} \ln \left(\frac{P_r^1 P_s^2}{P_{rs}} \right), \quad \text{and} \quad \text{(b)} \quad S \leq S_1 + S_2.$$

SOLUTION

(a) We have

$$P_r^1 = \sum_s P_{rs} \quad \text{(i)}$$

$$P_s^2 = \sum_r P_{rs} \quad \text{(ii)}$$

$$S_1 = -k \sum_r P_r^1 \ln P_r^1 \quad \text{(iii)}$$

$$S_2 = -k \sum_s P_s^2 \ln P_s^2 \quad \text{(iv)}$$

Using (i) in (iii)

$$S_1 = -k \sum_r \sum_s P_{rs} \ln P_r^1 \quad (\text{v})$$

Again using (ii) in (iv)

$$S_2 = -k \sum_r \sum_s P_{rs} \ln P_s^2 \quad (\text{vi})$$

Adding (v) and (vi)

$$S_1 + S_2 = -k \sum_r \sum_s \ln(P_r^1 P_s^2) \quad (\text{vii})$$

Again according to the question

$$S = -k \sum_r \sum_s P_{rs} \ln P_{rs} \quad (\text{viii})$$

[(viii) - (vii)] gives

$$S - (S_1 + S_2) = k \sum_r \sum_s P_{rs} \ln \frac{P_r^1 P_s^2}{P_{rs}} \quad (\text{Proved}) \quad (\text{ix})$$

(b) Using the inequality, $\ln x \leq x - 1$

$$\ln \frac{P_r^1 P_s^2}{P_{rs}} \leq \left(\frac{P_r^1 P_s^2}{P_{rs}} - 1 \right)$$

$$\Rightarrow P_{rs} \ln \frac{P_r^1 P_s^2}{P_{rs}} \leq P_{rs} \left(\frac{P_r^1 P_s^2}{P_{rs}} - 1 \right) = (P_r^1 P_s^2 - P_{rs}) \leq 0$$

$$\Rightarrow k \sum_r \sum_s P_{rs} \ln \frac{P_r^1 P_s^2}{P_{rs}} \leq 0$$

$$\Rightarrow [S - (S_1 + S_2)] \leq 0$$

$$\therefore S \leq (S_1 + S_2) \quad (\text{x})$$

PROBLEM 2.24: Consider a system of N very weakly interacting particles at a temperature T sufficiently high so that classical statistical mechanics is applicable. Each particle has mass m and is free to perform one-dimensional oscillation about its equilibrium position. Calculate the heat capacity of this system, if the restoring force is proportional to x^3 .

SOLUTION

The restoring force is given by

$$F = -Kx^3 \quad (\text{i})$$

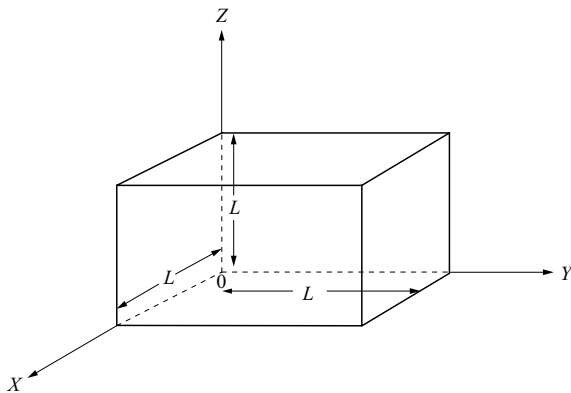
where K is the constant of proportionality.

Hence, the potential energy of a particle is

$$V = \frac{1}{4}Kx^3 \quad (\text{ii})$$

Therefore, the total energy of a particle is

$$\epsilon = \frac{p^2}{2m} + \frac{1}{4}Kx^3 \quad (\text{iii})$$



Now

$$\int_0^L e^{-\frac{mgz}{kT}} dz = \frac{kT}{mg} \left(1 - e^{-\frac{mgL}{kT}}\right)$$

and

$$\int_0^L ze^{-\frac{mgz}{kT}} dz = \left(\frac{kT}{mg}\right)^2 \left(1 - e^{-\frac{mgL}{kT}}\right) - \frac{kTL}{mg} e^{-\frac{mgL}{kT}}$$

$$\therefore \langle mgz \rangle = mg \times \frac{\left(\frac{kT}{mg}\right)^2 \left(1 - e^{-\frac{mgL}{kT}}\right) - \frac{kTL}{mg} e^{-\frac{mgL}{kT}}}{\frac{kT}{mg} \left(1 - e^{-\frac{mgL}{kT}}\right)} = kT - mgL \frac{e^{-\frac{mgL}{kT}}}{1 - e^{-\frac{mgL}{kT}}}$$

$$\Rightarrow \langle mgz \rangle = kT + mgL \left(1 - e^{-\frac{mgL}{kT}}\right)^{-1} \quad (\text{Ans.})$$

(ii)

The average kinetic energy of a molecule is given by

$$\left\langle \frac{p^2}{2m} \right\rangle = \frac{\int \frac{p^2}{2m} e^{-\beta\left(\frac{p^2}{2m} + mgz\right)} d^3 p d^3 r}{\int e^{-\beta\left(\frac{p^2}{2m} + mgz\right)} d^3 p d^3 r} = \frac{\int \frac{p^2}{2m} e^{-\frac{\beta p^2}{2m}} d^3 p}{\int e^{-\frac{\beta p^2}{2m}} d^3 p} = \frac{-\frac{\partial}{\partial \beta} \left[\left(\frac{2\pi m}{\beta}\right)^{\frac{3}{2}} \right]}{\left(\frac{2\pi m}{\beta}\right)^{\frac{3}{2}}} = \frac{3}{2\beta} = \frac{3}{2} kT \quad (\text{iii})$$

PROBLEM 2.26: Calculate the rotational partition function for heteronuclear and homonuclear molecules separately.

SOLUTION

The rotation of a diatomic molecule is specified by the angles (θ, ϕ) and the corresponding momenta (P_θ, P_ϕ) and its kinetic energy assumes the form

$$\epsilon_{rot} = \frac{P_\theta^2}{2I} + \frac{P_\phi^2}{2I \sin^2 \theta}.$$

For heteronuclear diatomic molecule:

$$\begin{aligned} \xi_{\text{heteronuclear}}^{\text{rot}} &= \frac{1}{h^2} \int e^{-\epsilon/kT} I dp_\theta dp_\phi d\theta d\phi \\ &= \frac{1}{h^2} \int_{\phi=0}^{2\pi} d\phi \int_{p_\phi=0}^{\infty} e^{-\frac{p_\phi^2}{2IkT}} dp_\phi \int_{\theta=0}^{\pi} d\theta \left[\int_{p_\theta=0}^{\infty} e^{-\frac{p_\theta^2}{2IkT \sin^2 \theta}} dp_\theta \right] \\ &= \frac{1}{h^2} \times 2\pi \times \frac{1}{2} \sqrt{2\pi IkT} \times \int_{\theta=0}^{\pi} d\theta \frac{1}{2} \sqrt{2\pi IkT} \sin \theta \\ \therefore \xi_{\text{heteronuclear}}^{\text{rot}} &= \frac{2\pi^2 IkT}{h^2} \end{aligned} \quad (\text{i})$$

For homonuclear diatomic molecule:

For homonuclear diatomic molecule, ϕ ranges from 0 to π (see Section 4.12.2).

$$\therefore \xi_{\text{homonuclear}}^{\text{rot}} = \frac{\pi^2 IkT}{h^2}$$

PROBLEM 2.27: Study the thermodynamics of a system of N non-interacting diatomic molecules, each having an electric dipole moment μ , placed in an external electric field \vec{E} . Assume that (i) the system is classical and (ii) $|\mu E| \ll kT$, where T is the absolute temperature of the system.

SOLUTION

The energy of a diatomic molecule in the presence of the electric field E is given by

$$\epsilon = \frac{P^2}{2m} + \left\{ \frac{P_\theta^2}{2I} + \frac{P_\phi^2}{2I \sin^2 \theta} \right\} - \mu E \cos \theta \quad (\text{i})$$

where I is the moment of inertia of the molecule.

Now the single particle canonical partition function is given by

$$\begin{aligned} \xi &= \frac{1}{h^3} \iiint \iiint \iiint e^{-\beta\epsilon} dr d\theta d\phi dp dp_\theta dp_\phi \\ \Rightarrow \xi &= \frac{1}{h^3} \left[\int_{r=0}^{V^{\frac{1}{3}}} dr \right] \times \left[\int_{\phi=0}^{2\pi} d\phi \right] \times \left[\int_{P=0}^{\infty} dp e^{-\frac{\beta p^2}{2m}} \right] \times \left[\int_{P_\theta=0}^{\infty} dp_\theta e^{-\frac{\beta p_\theta^2}{2m}} \right] \end{aligned} \quad (\text{ii})$$

$$\begin{aligned}
 & \times \left[\int_{\theta=0}^{\infty} d\theta e^{\beta\mu E \cos\theta} \left\{ \int_{p_\phi=0}^{\infty} dp_\phi e^{-\frac{\beta p_\phi^2}{2I \sin^2\theta}} \right\} \right] \\
 &= \frac{1}{h^3} V^{\frac{1}{3}} \times 2\pi \times \left(\frac{1}{2} \sqrt{\frac{2m\pi}{\beta}} \right) \times \left(\frac{1}{2} \sqrt{\frac{2I\pi}{\beta}} \right) \times \left(\int_{\theta=0}^{\infty} d\theta e^{\beta\mu E \cos\theta} \cdot \frac{1}{2} \sqrt{\frac{2I\pi}{\beta}} \sin\theta \right) \\
 &= \frac{\sqrt{2mI\pi^{\frac{5}{2}}}}{2h^3} \cdot \frac{1}{\beta^{\frac{3}{2}}} \cdot \int_0^\pi d\theta \sin\theta e^{\beta\mu E \cos\theta} \\
 &= \frac{\sqrt{2mI\pi^{\frac{5}{2}}}}{2h^3} \cdot \frac{1}{\beta^{\frac{3}{2}}} \cdot \frac{1}{\beta\mu E} \cdot (e^{\beta\mu E} - e^{-\beta\mu E}) \\
 \therefore \quad \xi &= \frac{\sqrt{2mI\pi^{\frac{5}{2}}}}{\mu E h^3} \frac{1}{\beta^{\frac{5}{2}}} \sinh(\beta\mu E) \tag{iii}
 \end{aligned}$$

Therefore, the canonical partition function of the system is

$$Z = \xi^N = \left[\frac{\sqrt{2mI\pi^{\frac{5}{2}}}}{\mu E h^3} \right]^N \left[\frac{\sinh \beta\mu E}{\beta^{\frac{5}{2}}} \right]^N \tag{iv}$$

$$\Rightarrow \ln Z = N \ln \left(\frac{\sqrt{2mI\pi^{\frac{5}{2}}}}{\mu E h^3} \right) + N \left[\ln \sinh \beta\mu E - \frac{5}{2} \ln \beta \right] \tag{v}$$

The mean energy of the system is given by

$$\bar{\epsilon} = -\frac{\partial \ln Z}{\partial \beta} = \frac{5}{2} \frac{N}{\beta} - N\mu E \coth(\beta\mu E) = \frac{5}{2} NkT - N\mu E \sinh\left(\frac{\mu E}{kT}\right) \tag{vi}$$

The specific heat at constant volume is given by

$$C_V = \left(\frac{\partial \bar{\epsilon}}{\partial T} \right)_V = \frac{5}{2} Nk - Nk \left(\frac{\mu E}{kT} \right)^2 \operatorname{cosec} h^2 \left(\frac{\mu E}{kT} \right) \tag{vii}$$

For $T \rightarrow 0$, i.e., $x \left(= \frac{\mu E}{kT} \right) \rightarrow \infty$

$$C_V \cong \frac{5}{2} Nk \left(\because \lim_{x \rightarrow \infty} \operatorname{cosec} hx = 0 \right) \tag{viii}$$

Now for $\mu E/kT \ll 1$, i.e., for high temperature

$$\operatorname{cosec} h^2 \left(\frac{\mu E}{kT} \right) \cong \frac{1}{\left(\frac{\mu E}{kT} \right)} - \frac{1}{3} + \frac{1}{15} \left(\frac{\mu E}{kT} \right)^2 \tag{ix}$$

and

$$\begin{aligned}
 \sum_3 &= \sum_{n=0}^{\infty} n^2 e^{-u(n+\frac{1}{2})} = e^{-\frac{u}{2}} \sum_{n=0}^{\infty} n^2 e^{-nu} \\
 &= e^{-\frac{u}{2}} [e^{-u} + 2^2 e^{-2u} + 3^2 e^{-3u} + \dots] \\
 &= e^{-\frac{u}{2}} \cdot e^{-u} [1 + 2^2 e^{-u} + 3^2 e^{-2u} + \dots] \\
 &= e^{-\frac{3u}{2}} \cdot \frac{(1 + e^{-u})}{(1 - e^{-u})^3}
 \end{aligned} \tag{iv}$$

Substituting (ii), (iii) and (iv) in (i)

$$\begin{aligned}
 \xi &= \frac{e^{-\frac{u}{2}}}{1 - e^{-u}} \left[1 + xu \left\{ \frac{e^{-u}(1 + e^{-u})}{(1 - e^{-u})^2} + \frac{e^{-u}}{(1 - e^{-u})} + \frac{1}{4} \right\} \right] \\
 &= \frac{e^{\frac{u}{2}}}{1 - e^{-u}} \left[1 + xu \left\{ \frac{2e^{-u}}{(1 - e^{-u})} + \frac{1}{4} \right\} \right]
 \end{aligned} \tag{v}$$

Therefore, the canonical partition function for the system is given by

$$Z = \xi^N$$

$$\Rightarrow \ln Z = N \ln \xi = N \left[-\frac{u}{2} - \ln(1 - e^{-u}) + \ln \left\{ 1 - xu \left(\frac{2e^{-u}}{(1 - e^{-u})} + \frac{1}{4} \right) \right\} \right] \tag{vi}$$

Then the internal energy of the system is

$$\begin{aligned}
 \bar{E} &= -\frac{\partial \ln Z}{\partial \beta} = kT^2 \frac{\partial \ln Z}{\partial T} = -hv \frac{\partial \ln Z}{\partial u} \\
 &= -N hv \left[-\frac{1}{2} - \frac{e^{-u}}{1 - e^{-u}} + \frac{x \left\{ 2 \left(\frac{e^{-u}}{1 - e^{-u}} \right)^2 - \frac{ue^{-u}}{(1 - e^{-u})^2} - \frac{2u(e^{-u})^2}{(1 - e^{-u})^3 + \frac{1}{4}} \right\}}{1 + xu \left\{ \frac{2e^{-u}}{(1 - e^{-u})} + \frac{1}{4} \right\}} \right] \\
 &= E_0 + E_{\text{correction}}
 \end{aligned} \tag{vii}$$

where

$$E_0 = \frac{1}{2} N hv + \frac{N hv}{e^u - 1} = \frac{1}{2} N hv + \frac{N hv}{e^{\frac{h\nu}{kT}} - 1} \tag{viii}$$

The corresponding specific heat at constant volume is

$$(C_V)_0 = \left(\frac{\partial E_0}{\partial T} \right)_V = Nk \left(\frac{hv}{kT} \right)^2 \frac{e^{\frac{h\nu}{kT}}}{\left[e^{\frac{h\nu}{kT}} - 1 \right]^2} \tag{ix}$$

$$E_{\text{correction}} = -x N hv \left[\frac{\left\{ 2 \left(\frac{e^{-u}}{1 - e^{-u}} \right)^2 - \frac{ue^{-u}}{(1 - e^{-u})^2} - \frac{2u(e^{-u})^2}{(1 - e^{-u})^3 + \frac{1}{4}} \right\}}{1 - xu \left\{ \frac{2e^{-u}}{(1 - e^{-u})} + \frac{1}{4} \right\}} \right] \tag{x}$$

Upto the first order in x , $\langle x \rangle$ reduces to

$$E_{\text{correction}} = -xN\hbar\nu \left[\frac{2e^{-u}}{(1-e^{-u})^2} - \frac{2ue^{-u}}{(1-e^{-u})^2} - \frac{4ue(e^{-u})^2}{(1-e^{-u})^3 + \frac{1}{4}} \right] \quad (\text{xi})$$

The corresponding specific heat is

$$(C_V)_{\text{correction}} = xNku^2 \frac{2e^{-u}}{(1-e^{-u})^2} + \frac{12u(e^{-u})^2}{(1-e^{-u})^4} - \frac{4(e^{-u})^2}{(1-e^{-u})^3 - \frac{4e^{-u}}{(1-e^{-u})^3}} \quad (\text{xii})$$

This is the correction to the specific heat upto the first order in x .

Comment: For $u (= \frac{\hbar\nu}{kT}) \ll 1$, i.e., for high temperature,

$$(C_V)_{\text{correction}} = xNk \times \frac{4}{u} = xNk \times \frac{4kT}{\hbar\nu} = x \left(\frac{4Nk^2}{\hbar\nu} \right) T \propto T,$$

which shows that the correction due to the anharmonicity increases with temperature, T .

PROBLEM 2.29: Calculate the canonical partition function and hence the specific heat at constant volume for a classical system of N non-interacting diatomic molecules enclosed in a box of volume V at temperature T .

SOLUTION

The energy of a diatomic molecule can be written as

$$E(\vec{p}_1, \vec{p}_2, \vec{r}_1, \vec{r}_2) = \frac{1}{2m} (p_1^2 + p_2^2) + \frac{1}{2}K |\vec{r}_1 - \vec{r}_2|^2 \quad (\text{i})$$

where $\vec{p}_1, \vec{p}_2, \vec{r}_1$ and \vec{r}_2 are the momenta and position coordinates of the two atoms in a diatomic molecule.

Let $\vec{R} = \frac{r_1 + r_2}{2}$ and $\vec{\rho} = \vec{r}_1 - \vec{r}_2$.

Then the Jacobian is

$$J = \begin{vmatrix} \frac{\partial \vec{r}_1}{\partial \vec{R}} & \frac{\partial \vec{r}_2}{\partial \vec{R}} \\ \frac{\partial \vec{r}_1}{\partial \vec{\rho}} & \frac{\partial \vec{r}_2}{\partial \vec{\rho}} \end{vmatrix} = \begin{vmatrix} 1 & 1 \\ \frac{1}{2} & -\frac{1}{2} \end{vmatrix} = -1 \Rightarrow |J| = 1 \quad (\text{ii})$$

$$\therefore d^3r_1 d^3r_2 = d^3R d^3\rho \quad (\text{iii})$$

Now the single particle canonical partition function is

$$\begin{aligned} \xi &= \int e^{-\beta H} d^3r_1 d^3r_2 d^3p_1 d^3p_2 = \int e^{-\beta H} d^3r_1 d^3r_2 d^3R d^3\rho \\ &= \left[\int e^{-\beta p_1^2} d^3p_1 \right] \left[\int e^{-\beta p_2^2} d^3p_2 \right] \left[\int d^3R \right] \left[\int e^{-\beta k \rho^2} d^3\rho \right] \\ &= \left(\frac{2\pi m}{\beta} \right)^{\frac{3}{2}} \times \left(\frac{2\pi m}{\beta} \right)^{\frac{3}{2}} \times V \times \left(\frac{2\pi}{\beta K} \right)^{\frac{3}{2}} \\ &= V \left(\frac{8\pi^3 m^2}{K} \right)^{\frac{3}{2}} \times \frac{1}{\beta^{\frac{9}{2}}} \end{aligned}$$

Therefore, the canonical partition function for the system is

$$Z = \xi^N = V^N \left(\frac{8\pi^3 m^2}{K} \right)^{\frac{3N}{2}} \times \frac{1}{\beta^{\frac{9N}{2}}} \quad (\text{iv})$$

$$\Rightarrow \ln Z = \ln \left[V^N \left(\frac{8\pi^3 m^2}{K} \right)^{\frac{3N}{2}} \right] - \frac{9N}{2} \ln \beta \quad (\text{v})$$

The mean energy of the system is

$$\bar{E} = -\frac{\partial \ln Z}{\partial \beta} = \frac{9N}{2\beta} = \frac{9}{2} NkT \quad (\text{vi})$$

Hence, the specific heat at constant volume is

$$C_V = \left(\frac{\partial \bar{E}}{\partial T} \right)_V = \frac{9}{2} Nk \quad (\text{vii})$$

PROBLEM 2.30: In Problem 2.31, calculate the mean square molecular diameter, $\langle |\vec{r}_1 - \vec{r}_2|^2 \rangle$.

SOLUTION

The mean square molecular diameter is

$$\begin{aligned} \langle |\vec{r}_1 - \vec{r}_2|^2 \rangle &= \frac{\int |\vec{r}_1 - \vec{r}_2|^2 e^{-\beta E} d^3 r_1 d^3 r_2 d^3 p_1 d^3 p_2}{\int e^{-\beta E} d^3 r_1 d^3 r_2 d^3 p_1 d^3 p_2} \\ &= \frac{\int \rho^2 e^{-\beta \left[\frac{1}{2m} (p_1^2 + p_2^2) + \frac{1}{2} K \rho^2 \right]} d^3 r_1 d^3 r_2 d^3 p_1 d^3 p_2}{\int e^{-\beta \left[\frac{1}{2m} (p_1^2 + p_2^2) + \frac{1}{2} K \rho^2 \right]} d^3 r_1 d^3 r_2 d^3 p_1 d^3 p_2} \\ &= \frac{\int \rho^2 e^{-\frac{1}{2} \beta K \rho^2} d^3 \rho}{\int e^{-\frac{1}{2} \beta K \rho^2} d^3 \rho} = \frac{\int_0^\infty \rho^4 e^{-\frac{1}{2} \beta K \rho^2} d\rho}{\int_0^\infty \rho^2 e^{-\frac{1}{2} \beta K \rho^2} d\rho} = \frac{2kT}{K} \frac{\int_0^\infty x^{\frac{3}{2}} e^{-x} dx}{\int_0^\infty x^{\frac{1}{2}} e^{-x} dx} = \frac{2kT}{K} \frac{\Gamma\left(\frac{5}{2}\right)}{\Gamma\left(\frac{3}{2}\right)} = \frac{3kT}{K} \\ \langle |\vec{r}_1 - \vec{r}_2|^2 \rangle &\propto T. \end{aligned}$$

PROBLEM 2.31: Consider a classical system of N non-interacting diatomic molecules enclosed in a box of volume V and temperature T . The energy for a single molecule is $E(\vec{p}_1, \vec{p}_2, \vec{r}_1, \vec{r}_2) = \frac{1}{2m} (p_1^2 + p_2^2) + \varepsilon |r_{12} - r_0|$, where $\vec{p}_1, \vec{p}_2, \vec{r}_1$ and \vec{r}_2 are the momenta and position coordinates of the two atoms in a molecule. ε and r_0 are given positive constants and $r_{12} = |\vec{r}_1 - \vec{r}_2|$. Find the specific heat of the system at a constant volume as a function of temperature.

SOLUTION

The energy of a molecule is

$$E(\vec{p}_1, \vec{p}_2, \vec{r}_1, \vec{r}_2) = \frac{1}{2m} (p_1^2 + p_2^2) + \varepsilon|r_{12} - r_0| \quad (\text{i})$$

Let $\vec{R} = \frac{\vec{r}_1 + \vec{r}_2}{2}$ and $\vec{\rho} = \vec{r}_1 - \vec{r}_2$.

Then the Jacobian is

$$J = \begin{vmatrix} \frac{\partial \vec{r}_1}{\partial \vec{R}} & \frac{\partial \vec{r}_2}{\partial \vec{R}} \\ \frac{\partial \vec{r}_1}{\partial \vec{\rho}} & \frac{\partial \vec{r}_2}{\partial \vec{\rho}} \end{vmatrix} = \begin{vmatrix} 1 & 1 \\ \frac{1}{2} & -\frac{1}{2} \end{vmatrix} = -1 \Rightarrow |J| = 1 \quad (\text{ii})$$

$$\therefore d^3 r_1 d^3 r_2 = d^3 R d^3 \rho \quad (\text{iii})$$

The single particle canonical partition function is

$$\begin{aligned} \xi &= \int e^{-\beta H} d^3 r_1 d^3 r_2 d^3 p_1 d^3 p_2 = \int e^{-\beta H} d^3 r_1 d^3 r_2 d^3 R d^3 \rho \\ &= \left[\int e^{-\frac{\beta p_1^2}{2m}} d^3 p_1 \right] \times \left[\int e^{-\frac{\beta p_2^2}{2m}} d^3 p_2 \right] \times \left[\int d^3 R \right] \times \left[\int \rho^{-\beta \varepsilon |\rho - r_0|} d^3 \rho \right] \\ &= \left[4\pi \left(\frac{2m}{\beta} \right)^{\frac{3}{2}} \frac{1}{2} \tau \left(\frac{3}{2} \right) \right] \times \left[4\pi \left(\frac{2m}{\beta} \right)^{\frac{3}{2}} \frac{1}{2} \tau \left(\frac{3}{2} \right) \right] \times V \times \left[\frac{4\pi}{(\beta \varepsilon)^3} \int_0^\infty y^2 e^{-|y-x|} dy \right] \end{aligned} \quad (\text{iv})$$

where $y = \beta \varepsilon \rho$ and $x = \beta \varepsilon r_0$.

Now

$$\int y^2 e^{-y} dy = y^2 e^{-y} - \int 2y e^{-y} dy + 2 \int e^{-y} dy = y^2 e^{-y} - 2y e^{-y} + 2e^{-y} \quad (\text{v})$$

Similarly,

$$\int y^2 e^{-y} dy = -y^2 e^{-y} - 2y e^{-y} + 2e^{-y} \quad (\text{vi})$$

$$\therefore \int_x^\infty y^2 e^{-y} dy = x^2 e^{-x} + 2x e^{-x} + 2e^{-x} \quad (\text{vii})$$

Again

$$\begin{aligned} \int_0^\infty y^2 e^{-|y-x|} dy &= \int_0^x y^2 e^{-(y-x)} dy + \int_x^\infty y^2 e^{-(y-x)} dy = e^{-x} \int_0^x y^2 e^{-y} dy + e^x \int_x^\infty y^2 e^{-y} dy \\ &= e^x [x^2 e^x - 2x e^x + 2e^x - 2] + e^x [x^2 e^{-x} + 2x e^{-x} + 2e^{-x}] \end{aligned} \quad (\text{viii})$$

$$\therefore \int_0^\infty y^2 e^{-|y-x|} dy = 2x^2 + 4 - 2e^{-x} \quad (\text{ix})$$

Now, when the cylinder is rotated, it becomes energetically favourable for the molecules to move towards the edge of the cylinder, so we expect the density to increase with radius r .

In a frame of reference rotating with a gas, a molecule of mass m at a distance r from the axis experiences a centrifugal force

$$F_c = m\omega^2 r \quad (\text{ii})$$

away from the axis.

∴ The centrifugal potential energy is

$$V_c = -\frac{1}{2}m\omega^2 r^2 \quad (\text{iii})$$

From the Boltzmann distribution law, we expect the probability of a molecule to be proportional to $\exp\left(-\frac{V_c}{kT}\right)$ and so we can write

$$\sigma(r) = A \exp\left(\frac{m\omega^2 r}{2kT}\right) \quad (\text{iv})$$

where A is a constant of proportionality.

Now the total mass of the gas within the cylinder is given by

$$M = 2\pi L \int_0^a \sigma(r) r dr = 2\pi L A \int_0^a r \exp\left(\frac{m\omega^2 r^2}{2kT}\right) dr \quad (\text{v})$$

The integral can be easily evaluated by noting that

$$\frac{d}{dr} \left[\exp\left(\frac{m\omega^2 r^2}{2kT}\right) \right] = \frac{m\omega^2 r}{kT} \exp\left(\frac{m\omega^2 r^2}{2kT}\right) \quad (\text{vi})$$

$$\therefore M = \frac{2\pi L A kT}{m\omega^2} \left[\exp\left(\frac{m\omega^2 a^2}{2kT}\right) - 1 \right] \quad (\text{vii})$$

Equating (i) and (vii), we have the expression for A :

$$A = \frac{\sigma_0 m \omega^2 a^2}{2kT} \frac{1}{\left[\exp\left(\frac{m\omega^2 a^2}{2kT}\right) - 1 \right]} \quad (\text{viii})$$

Using (viii), we get the expression for $\sigma(r)$ as

$$\sigma(r) = \frac{\sigma_0 m \omega^2 a^2}{2kT} \frac{\exp\left(\frac{m\omega^2 r^2}{2kT}\right)}{\left[\exp\left(\frac{m\omega \left[\exp\left(\frac{m\omega^2 a^2}{2kT}\right) - 1 \right]^2 a^2}{2kT}\right) - 1 \right]} \quad (\text{ix})$$

Let $R = \frac{r}{a}$ and $\Omega = \frac{m\omega^2 a^2}{2kT}$.

$$\therefore \frac{\sigma(R)}{\sigma_0} = \Omega \frac{\exp(\Omega R^2)}{[\exp(\Omega) - 1]} \quad (\text{x})$$

Writing the function as a series expansion, we have

$$\frac{\sigma(R)}{\sigma_0} = \Omega \frac{(1 + \Omega R^2 + \frac{1}{2!} \Omega^2 R^4 + \dots)}{\Omega + \frac{1}{2!} (\Omega^2 + \dots)} = \frac{(1 + \Omega + \frac{1}{2!} \Omega^2 + \dots)}{(1 + \frac{\Omega}{2} + \dots)} \quad (\text{xi})$$

For small ω (i.e., for small Ω), we can write (xi) approximately as

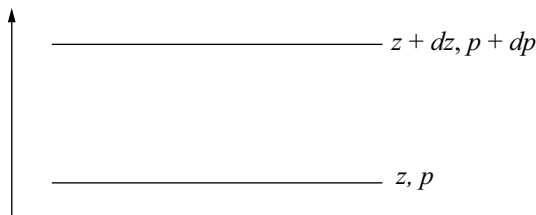
$$\frac{\sigma(R)}{\sigma_0} \cong \frac{(1 + \Omega R^2)}{(1 + \frac{\Omega}{2})} \quad (\text{xii})$$

which shows that $\sigma(R) = \sigma_0$, i.e., the density remains unchanged when $R^2 = \frac{1}{2} \Rightarrow \frac{r^2}{a^2} = \frac{1}{2} \Rightarrow r = \frac{a}{\sqrt{2}}$. Thus for small ω , the density remains unchanged at a distance $\frac{a}{\sqrt{2}}$ from the axis of the cylinder.

PROBLEM 2.33: Consider an ideal gas at absolute temperature T in a uniform gravitational field described by acceleration g . By writing the condition of hydrostatic equilibrium for a slice of the gas located between heights z and $z + dz$, derive an expression for $n(z)$, the number of molecules per cm^3 at height z . Also show that this result is identical with that derived from statistical mechanics.

SOLUTION

Let us consider a slice between heights z and $z + dz$. Let the pressure at z be p and that at $z + dz$ be $p + dp$.



Then for hydrostatic equilibrium,

$$pA - (p + dp)A = mngAdz \quad (\text{i})$$

where, A = cross-sectional area of the slice

n = number density

m = particle mass

g = acceleration due to gravity.

$$\therefore dp = -mngdz \quad (\text{ii})$$

Again treating the gas as an ideal gas, we can write

$$p = nkT \Rightarrow dp = kTdn \quad (\text{iii})$$

Using (iii) in (ii), we have

$$\frac{dn}{n} = -\frac{mg}{kT} dz$$

On integration

$$\ln n = -\frac{mg}{kT}z + \text{constant} \quad (\text{iv})$$

Let at $z = 0, n = n(0)$.

$$\therefore n = n(0)e^{-\frac{mgz}{kT}} \quad (\text{v})$$

Using ideal gas law: $p = nkT, p(0) = n(0)kT$

$$p = p(0)e^{-\frac{mgz}{kT}} \quad (\text{vi})$$

Now the probability $P(\vec{r}, \vec{p}) d^3r d^3p$ that the molecule has position lying in the range between \vec{r} and $\vec{r} + d\vec{r}$ and momentum in the range between \vec{p} and $\vec{p} + d\vec{p}$ is given by

$$P(\vec{r}, \vec{p}) d^3r d^3p \propto \frac{d^3r d^3p}{h^3} e^{-\beta\left(\frac{p^2}{2m} + mgz\right)} \quad (\text{vii})$$

Therefore, the probability $P(z) dz$ that a molecule is located at a height between z and $z + dz$ is

$$P(z) dz \propto \frac{1}{h^3} \times \left[\int_{(x,y)} dx dy \right] \times \left[\int_{p=0}^{\infty} \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} e^{-\beta\frac{p^2}{2m}} P^2 \sin\theta dp d\theta d\phi \right] \times e^{-\beta mgz} dz \quad (\text{viii})$$

But $\int_{(x,y)} dx dy = A$, cross-sectional area of the slice.

$$\therefore P(z) dz = \text{constant} \times \frac{A}{h^3} \left(\frac{2\pi m}{\beta} \right)^{3/2} e^{-\frac{mg}{kT}z} \quad (\text{ix})$$

Let at $z = 0, P(z)|_{z=0} = P(0)$.

$$\therefore P(0) = \text{constant} \times \frac{A}{h^3} \left(\frac{2\pi m}{\beta} \right) \quad (\text{x})$$

$$\Rightarrow P(z) = P(0)e^{-\frac{mg}{kT}z} \quad (\text{xi})$$

Thus, the probability of finding a molecule at height z decreases exponentially with height.

Now

$$n(z) dz \propto p(z) dz = \text{constant} \times P(0)e^{-\frac{mgz}{kT}} dz \quad (\text{xii})$$

At $z = 0, n = n(0) \Rightarrow \text{constant} \times P(0) = n(0)$

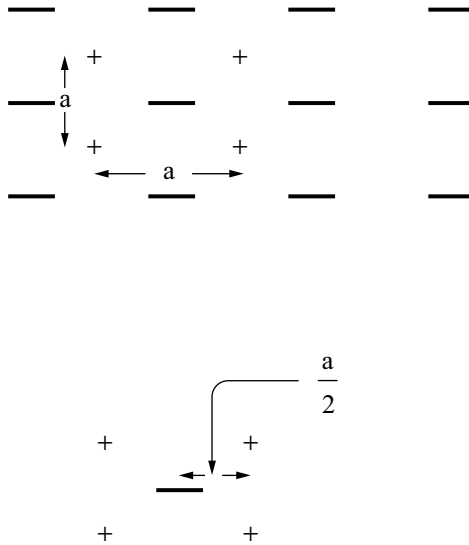
$$\therefore n(z) = n(0)e^{-\frac{mgz}{kT}} \quad (\text{xiii})$$

which is same as (v).

PROBLEM 2.34: Consider a system consists of N weakly interacting particles, each of which can be in either of two states with respective energies ε_1 and ε_2 ($\varepsilon_2 > \varepsilon_1$). Calculate explicitly the mean energy \bar{E} and heat capacity C_V of this system.

SOLUTION

Consider a pair of one +ve and one -ve particle.



The adjoining figure shows that there are 4 possible states of this pair. Since the potential energy of a charged particle of charge in an external electric field is $V(x) = -e\epsilon x$, the average separation between a +ve ion and a -ve ion is given by

$$\langle x \rangle = \frac{2 \cdot \frac{a}{2} e^{\beta \frac{a}{2} \epsilon e} - 2 \cdot \frac{a}{2} e^{-\beta \frac{a}{2} \epsilon e}}{2e^{\beta \frac{a}{2} \epsilon e} + 2e^{-\beta \frac{a}{2} \epsilon e}} = \frac{a}{2} \tanh \frac{\beta e \epsilon a}{2} \quad (\text{i})$$

If there are N number of pairs per unit volume, the electric polarization or average dipole moment per unit volume is given by

$$\langle \mu \rangle = Ne \langle x \rangle = Ne \frac{a}{2} \tanh \frac{\beta e \epsilon a}{2} \quad (\text{ii})$$

PROBLEM 2.36: Calculate the canonical partition function and hence the specific heat of a classical ideal two-dimensional gas.

SOLUTION

The energy of a single particle is

$$\epsilon = \frac{p_x^2 + p_y^2}{2m} \quad (\text{i})$$

Then the single particle canonical partition function is

$$\begin{aligned} \xi &= \frac{1}{h^2} \int e^{-\frac{\beta}{2m}(p_x^2 + p_y^2)} dx dy dp_x dp_y = \frac{A}{h^2} \left[\int_{-\infty}^{\infty} e^{-\frac{\beta p_x^2}{2m}} dp_x \right] \times \left[\int_{-\infty}^{\infty} e^{-\frac{\beta p_y^2}{2m}} dp_y \right] \\ &= \frac{A}{h^2} \left(\frac{2\pi m}{\beta} \right) \end{aligned} \quad (\text{ii})$$

where A is the area.

Hence, the canonical partition function of the system is given by

$$Z = \frac{A^N}{h^{3N}} \left(\frac{2m\pi}{\beta} \right)^N \quad (\text{iii})$$

The mean energy of the system is

$$\bar{E} = - \left(\frac{\partial \ln Z}{\partial \beta} \right)_V = NkT$$

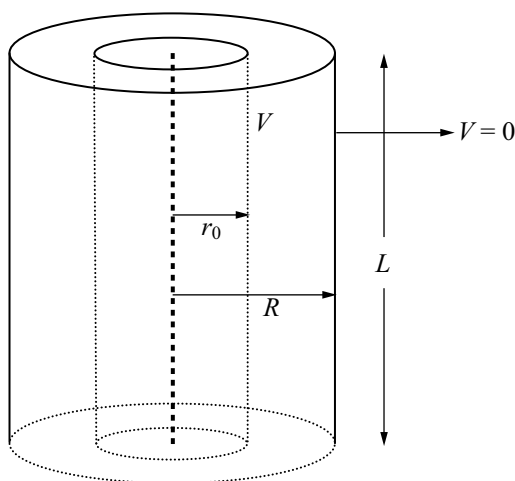
∴ The specific heat at constant volume is

$$C_V = \left(\frac{\partial \bar{E}}{\partial T} \right)_V = Nk \quad (\text{iv})$$

PROBLEM 2.37: Suppose that a wire of radius r_0 is placed along the axis of a metal cylinder of radius R and length L . The wire is maintained at a positive potential V with respect to the cylinder and the whole system is at some high absolute temperature T . As a result, electrons emitted from the hot metals form a dilute gas filling the cylindrical container and in equilibrium with it. The density of these electrons is so low that their mutual electrostatic interaction can be neglected.

Use Gauss' theorem, obtain an expression for the electrostatic potential at a radial distance r from the wire ($r_0 < r < R$). [Assume the cylinder to be infinitely long so that end effects are neglected.] Also find the density of the electron gas filling the space between the wire and cylinder, as a function of the radial distance in equilibrium.

SOLUTION



SOLUTION

In the rotating frame of reference, the molecules feel a centrifugal force $m\omega^2 r$ radially outward. This force can be obtained from a potential

$$F_r = m\omega^2 r \hat{r} = -\frac{\sigma V}{\sigma r} \hat{r} \quad (\text{i})$$

where \hat{r} is the unit vector in the radial direction.

Therefore, the potential energy of a molecule in the rotating frame is

$$V = -\frac{1}{2}m\omega^2 r^2 \quad (\text{ii})$$

so that the total energy of a molecule in the rotating frame is given by

$$\varepsilon = \frac{p^2}{2m} + \left(-\frac{1}{2}m\omega^2 r^2\right) \quad (\text{iii})$$

The probability of finding the molecule in the energy range ε to $\varepsilon + d\varepsilon$ is then given by

$$P(\varepsilon) = \frac{1}{Z} e^{\frac{p^2}{2mkT}} e^{\frac{m\omega^2 r^2}{2kT}} \quad (\text{iv})$$

Then the probability of finding the molecule between r and $r + dr$ is obtained by integrating over all the other coordinates and is given by

$$P(r)dr = P(0)e^{\frac{m\omega^2 r^2}{2kT}} dr \quad (\text{v})$$

where $P(0)$ is a constant which correctly normalizes the distribution.

Equation (v) is the radial distribution of molecules. As expected, the molecules crowd towards the larger radii. It should be noted that we have taken the rotating speed to be very high so that the effect of the Coriolis force is ignored.

Now from (v), the concentration at r_1 is

$$\sigma(r_1) \propto e^{-\frac{m\omega^2 r_1^2}{2kT}} \quad (\text{vi})$$

Similarly,

$$\sigma(r_2) \propto e^{-\frac{m\omega^2 r_2^2}{2kT}}$$

$$\therefore \frac{\sigma(r_1)}{\sigma(r_2)} = e^{\frac{1}{2} \frac{m\omega^2 (r_1^2 - r_2^2)}{kT}} \quad (\text{vii})$$

$$\Rightarrow m = \frac{2kT}{\omega^2 (r_1^2 - r_2^2)} \ln \left[\frac{\sigma(r_1)}{\sigma(r_2)} \right]$$

PROBLEM 2.40: In order to measure a certain physical quantity, it is necessary to know the equilibrium θ_0 of a torsional pendulum. θ_0 is determined by the minimum in the potential energy of the pendulum $V(\theta) = \frac{1}{2}K(\theta - \theta_0)^2$. The pendulum, when rotating, has a kinetic energy $T = \frac{1}{2}I\dot{\theta}^2$, where $\theta = d\theta/dt$. The precision with which θ_0 can be found is limited because the pendulum is in thermal equilibrium with its environment at a temperature T .

- (b) The degeneracy of the n th energy level is n^2 . The partition function for a single atom, neglecting the unbound states, is

$$Z = \sum_{\text{states}} \exp\left(-\frac{\epsilon_i}{kT}\right) = \sum_{n=1}^{\infty} n^2 \exp\left(\frac{\alpha}{n^2}\right) \quad (\text{iii})$$

where $\alpha = A/kT$. Since $\alpha > 0$, it follows that $\exp(\alpha/n^2) > 1$ for all n . Using this, we can set the lower bound of Z , but Z diverges since the lower bound diverges.

$$\therefore Z > \sum_{n=1}^{\infty} n^2, \text{ which diverges.}$$

2.3 GRAND CANONICAL ENSEMBLE

It is a collection of large number of essentially independent systems, having **same temperature T , volume V and chemical potential μ** . Thus, the individual systems of a grand canonical ensemble are separated by rigid, permeable and conducting walls.

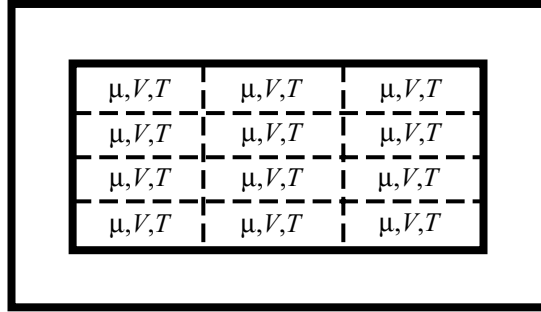


Fig. 2.7. Grand canonical ensemble.

As the separating walls are conducting and permeable, the exchange of heat energy as well as that of particles between the systems take place in such a way that all the systems arrive at common temperature T and the chemical potential μ .

2.3.1 Probability distribution and grand canonical partition function

Let us consider a system R of fixed volume V in contact with a large reservoir R' with which the system can exchange not only energy, but particles also. **We wish to find the probability P_r of finding the system R in any one particular microstate r of energy E_r .**

Neither the energy E_r of R nor the number of particles N_r in R are fixed, but the total energy E^0 and total number of particles N^0 of the combined system $R^0 = R + R'$ are fixed, i.e.,

$$\begin{aligned} E_r + E' &= E^0 = \text{constant} \\ N_r + N' &= N^0 = \text{constant} \end{aligned} \quad (2.3.1)$$

where E' and N' denote the energy and number of particles in the reservoir R' respectively.

Let $\Omega'(E'N')$ denote the number of states accessible to R' , when it contains N' particles and has an energy in the range near E' . Then if R is in a particular state r , the number of states accessible to the combined system R^0 is $1 \times \Omega'(E', N') = \Omega'(E^0 - E_r, N^0 - N_r)$. Hence, the probability of finding the system R in this state is

$$P_r = \frac{1 \times \Omega'(E^0 - E_r, N^0 - N_r)}{\Omega_{\text{total}}^0} \quad (2.3.2)$$

where Ω_{total}^0 is the total number of states accessible to the combined system R^0 . It is independent of r and is just a constant. Writing $\frac{1}{\Omega_{\text{total}}^0} = c' = \text{constant}$,

$$P_r = c' \Omega'(E^0 - E_r, N^0 - N_r) \quad (2.3.3)$$

Taking logarithms on both sides

$$\ln P_r = \ln c' + \ln \Omega'(E^0 - E_r, N^0 - N_r) \quad (2.3.4)$$

Since R is very small compared to R' , $E_r \ll E^0$ and $N_r \ll N^0$, expanding $\ln \Omega'(E', N')$ = $\ln \Omega'(E^0 - E_r, N^0 - N_r)$ about $E' = E^0$ and $N' = N^0$, we have

$$\ln \Omega'(E^0 - E_r, N^0 - N_r) = \ln \Omega'(E^0, N^0) - \left[\frac{\partial \ln \Omega'}{\partial E'} \right]_{E^0} E_r - \left[\frac{\partial \ln \Omega'}{\partial N'} \right]_{N^0} N_r \dots$$

Since $E_r \ll E^0$ and $N_r \ll N^0$, we can neglect the higher order terms and so we have

$$\ln \Omega'(E^0 - E_r, N^0 - N_r) = \ln \Omega'(E^0, N^0) - \left[\frac{\partial \ln \Omega'}{\partial E'} \right]_{E^0} E_r - \left[\frac{\partial \ln \Omega'}{\partial N'} \right]_{N^0} N_r \quad (2.3.5)$$

The derivatives are evaluated for $E' = E^0$ and $N' = N^0$ and so they are constants, characterizing the reservoir R' . We write $\left[\frac{\partial \ln \Omega'}{\partial E'} \right]_{E^0} = \beta$ and $\left[\frac{\partial \ln \Omega'}{\partial N'} \right]_{N^0} = \alpha$.

Then equation (2.3.5) becomes

$$\ln \Omega'(E^0 - E_r, N^0 - N_r) = \ln \Omega'(E^0, N^0) - \beta E_r - \alpha N_r \quad (2.3.6)$$

$$\Rightarrow \Omega'(E^0 - E_r, N^0 - N_r) = \Omega'(E^0, N^0) e^{-\beta E_r - \alpha N_r}$$

Using equation (2.3.6), equation (2.3.3) becomes

$$P_r = c' \Omega'(E^0, N^0) e^{-\beta E_r - \alpha N_r}$$

$$\boxed{\Rightarrow P_r = c e^{-\beta E_r - \alpha N_r}} \quad (2.3.7)$$

where $c = c' \Omega'(E^0, N^0)$, constant of proportionality, independent of r .

Equation (2.3.7) is called the **grand canonical** distribution. An ensemble of systems, distributed according to this probability distribution, is called a **grand canonical ensemble**.

The parameter β is the temperature parameter of the reservoir. $\beta = 1/kT$, where T is the absolute temperature of the reservoir and $\mu = -kT\alpha$, the chemical potential of the reservoir.

$$\therefore P_r = c e^{\mu \beta N_r - \beta E_r} \quad (2.3.8)$$

The normalization condition for probabilities demands $\sum_r P_r = 1$. Applying this to equation (2.3.8),

we have $c = \frac{1}{\sum_r e^{\mu\beta N_r - \beta E_r}}$ and so

$$P_r = \frac{e^{\mu\beta N_r - \beta E_r}}{\sum_r e^{\mu\beta N_r - \beta E_r}} = \frac{e^{\mu\beta N_r - \beta E_r}}{Z(\mu, V, T)} \quad (2.3.9)$$

where $Z(\mu, V, T) = \sum_r e^{\mu\beta N_r - \beta E_r} \rightarrow$ **grand canonical partition function.**

2.3.2 Density and energy fluctuations in grand canonical ensemble

In this case, fluctuations in both E and N are present.

Let \bar{N} be the average number of particles of the system R . Then the mean square deviation in it is given by

$$\overline{(\Delta N)^2} = \overline{(N - \bar{N})^2} = \overline{N^2} - \bar{N}^2$$

Now

$$\bar{N} = \frac{\sum_r N_r P_r}{\sum_r P_r} = \sum_r N_r P_r = \frac{\sum_r N_r e^{\mu\beta N_r - \beta E_r}}{\sum_r e^{\mu\beta N_r - \beta E_r}}.$$

The grand canonical partition function is

$$Z(\mu, V, T) = \sum_r e^{\mu\beta N_r - \beta E_r} \Rightarrow \frac{1}{\beta} \frac{\partial Z}{\partial \mu} = \sum_r N_r e^{\mu\beta N_r - \beta E_r}.$$

$$\therefore \bar{N} = \frac{1}{\beta} \frac{1}{Z} \frac{\partial Z}{\partial \mu} = \frac{1}{\beta} \frac{\partial \ln Z}{\partial \mu}$$

Again

$$\overline{N^2} = \frac{\sum_r N_r^2 P_r}{\sum_r P_r} = \sum_r N_r^2 P_r = \frac{\sum_r N_r^2 e^{\mu\beta N_r - \beta E_r}}{\sum_r e^{\mu\beta N_r - \beta E_r}} = \frac{\sum_r N_r^2 e^{\mu\beta N_r - \beta E_r}}{Z(\mu, V, T)} = \frac{1}{Z} \frac{1}{\beta^2} \frac{\partial^2 Z}{\partial \mu^2}$$

$$\text{Hence, } \overline{(\Delta N)^2} = \frac{1}{\beta^2} \frac{1}{Z} \frac{\partial^2 Z}{\partial \mu^2} - \left(\frac{1}{\beta} \frac{1}{Z} \frac{\partial Z}{\partial \mu} \right)^2 = \frac{1}{\beta} \frac{\partial}{\partial \mu} \left(\frac{1}{\beta} \frac{1}{Z} \frac{\partial Z}{\partial \mu} \right) = kT \frac{\partial \bar{N}}{\partial \mu}.$$

\therefore The root mean square fluctuation in N is

$$\Delta^* N = \left[\overline{(\Delta N)^2} \right]^{1/2} = \left[kT \frac{\partial \bar{N}}{\partial \mu} \right]_{T,V}^{1/2}.$$

The relative fluctuation in N is then

$$\frac{\Delta^* N}{\bar{N}} = \frac{1}{\bar{N}} \left[kT \frac{\partial \bar{N}}{\partial \mu} \right]_{T,V}^{1/2} \quad (2.3.10)$$

and

$$\begin{aligned}\bar{E}^2 &= \frac{\sum_r E_r^2 e^{\mu\beta N_r - \beta E_r}}{\sum_r e^{\mu\beta N_r - \beta E_r}} = \frac{\sum_r E_r^2 e^{\mu\beta N_r - \beta E_r}}{Z(\mu, V, T)} \\ &= \frac{1}{Z} \left(\frac{\partial^2 Z}{\partial \beta^2} \right)_{\mu, V} = \frac{\partial}{\partial \beta} \left(\frac{1}{Z} \frac{\partial Z}{\partial \beta} \right) + \frac{1}{Z^2} \left(\frac{\partial Z}{\partial \beta} \right)^2 \\ &= \frac{\partial}{\partial \beta} \left(\frac{\partial \ln Z}{\partial \beta} \right) + \left(\frac{\partial \ln Z}{\partial \beta} \right)^2 = -\frac{\partial \bar{E}}{\partial \beta} + (\bar{E})^2\end{aligned}$$

$$\therefore \overline{(\Delta E)^2} = \bar{E}^2 - \bar{E}^2 = -\left(\frac{\partial \bar{E}}{\partial \beta} \right)_{\mu, V} = kT^2 \left(\frac{\partial \bar{E}}{\partial T} \right)_{\mu, V}$$

and

$$\bar{N} = \frac{1}{\beta} \left(\frac{\partial \ln Z}{\partial \mu} \right)_{V, T} = -\left(\frac{\partial \ln Z}{\partial (-\mu\beta)} \right)_{V, T} \quad (2.3.14)$$

Eliminating μ from (2.3.13) and (2.3.14), we see that $\bar{E} = \bar{E}(\bar{N}, V, T)$, so that

$$\left(\frac{\partial \bar{E}}{\partial T} \right)_{\mu, V} = \left(\frac{\partial \bar{E}}{\partial T} \right)_{\bar{N}, V} + \left(\frac{\partial \bar{E}}{\partial \bar{N}} \right)_{T, V} \times \left(\frac{\partial \bar{N}}{\partial T} \right)_{\mu, V} = C_V + \left(\frac{\partial \bar{E}}{\partial \bar{N}} \right)_{T, V} \times \left(\frac{\partial \bar{N}}{\partial T} \right)_{\mu, V}$$

where $C_V = \left(\frac{\partial \bar{E}}{\partial T} \right)_{\bar{N}, V}$, the specific heat of the system at constant volume.

$$\therefore \overline{(\Delta E)^2} = kT^2 \left[C_V + \left(\frac{\partial \bar{E}}{\partial \bar{N}} \right)_{T, V} \left(\frac{\partial \bar{N}}{\partial T} \right)_{\mu, V} \right]$$

Again from equation (2.3.13)

$$\left(\frac{\partial \bar{E}}{\partial (-\mu\beta)} \right)_{V, T} = \left(\frac{\partial \bar{N}}{\partial \beta} \right)_{\mu, V} \text{ and hence } \left(\frac{\partial \bar{N}}{\partial T} \right)_{\mu, V} = \frac{1}{T} \left(\frac{\partial \bar{E}}{\partial \mu} \right)_{T, V}.$$

$$\begin{aligned}\therefore \overline{(\Delta E)^2} &= kT^2 \left[C_V + \frac{1}{T} \times \left(\frac{\partial \bar{E}}{\partial \bar{N}} \right)_{T, V} \left(\frac{\partial \bar{E}}{\partial \mu} \right)_{T, V} \right] \\ &= kT^2 C_V + kT \left(\frac{\partial \bar{E}}{\partial \bar{N}} \right)_{T, V} \left(\frac{\partial \bar{E}}{\partial \mu} \right)_{T, V} \\ &= kT^2 C_V + kT \left(\frac{\partial \bar{E}}{\partial \bar{N}} \right)_{T, V}^2 \left(\frac{\partial \bar{N}}{\partial \mu} \right)_{T, V}\end{aligned}$$

$$\text{But } \overline{(\Delta N)^2} = kT \left(\frac{\partial \bar{N}}{\partial \mu} \right)_{T, V}.$$

$$\therefore \overline{(\Delta E)^2} = kT^2 C_V + \left(\frac{\partial \bar{E}}{\partial \bar{N}} \right)_{T, V}^2 \overline{(\Delta N)^2} = \overline{(\Delta E)^2}_{\text{canonical}} + \left(\frac{\partial \bar{E}}{\partial \bar{N}} \right)_{T, V}^2 \overline{(\Delta N)^2} \quad (2.3.15)$$

This is the desired result, which says that the mean square fluctuation in the energy E of a system in the grand canonical ensemble is equal to the value it would have in the canonical ensemble plus a contribution arising due to the fluctuation in the particle number. Under ordinary circumstances, the relative fluctuation in the energy of the system is negligible. However, in the region of phase transition, the fluctuation in the energy is large because of the second term.

2.3.3 Thermodynamic quantities in terms of the grand canonical partition function

1. Internal energy

This is given by

$$\bar{E} = - \left(\frac{\partial \ln Z}{\partial \beta} \right)_{\mu, V} = kT^2 \left(\frac{\partial \ln Z}{\partial T} \right)_{\mu, V} \quad (2.3.16)$$

2. Specific heat

The specific heat at constant volume is given by

$$C_V = \left(\frac{\partial \bar{E}}{\partial T} \right)_{\bar{N}, V} \quad (2.3.17)$$

where \bar{E} is given by (2.3.16).

3. Thermodynamic pressure

The grand canonical partition function is $Z = Z(\mu, V, T)$. For the sake of convenience, let us write Z as a function of $\alpha (= -\mu\beta)$, V and $\beta (= 1/kT)$, i.e., $Z = Z(\alpha, V, \beta)$.

$$\therefore d \ln Z(\mu, V, T) = d \ln Z(\alpha, V, \beta) = \left(\frac{\partial \ln Z}{\partial \alpha} \right) d\alpha + \left(\frac{\partial \ln Z}{\partial V} \right) dV + \left(\frac{\partial \ln Z}{\partial \beta} \right) d\beta \quad (2.3.18)$$

Now

$$\bar{N} = \frac{1}{\beta} \left(\frac{\partial \ln Z}{\partial \mu} \right)_{V, T} = - \left(\frac{\partial \ln Z}{\partial \alpha} \right)_{V, T} \quad (2.3.19)$$

Using (2.3.16) and (2.3.19) in (2.3.18)

$$\begin{aligned} d \ln Z &= -\bar{N} d\alpha + \left(\frac{\partial \ln Z}{\partial V} \right) dV - \bar{E} d\beta \\ \Rightarrow d [\ln Z + \bar{N}\alpha + \bar{E}\beta] &= \alpha d\bar{N} + \beta d\bar{E} + \left(\frac{\partial \ln Z}{\partial V} \right) dV \\ \Rightarrow d \left[k \left\{ \ln Z - \frac{\bar{N}\mu}{kT} + \frac{\bar{E}}{kT} \right\} \right] &= \frac{1}{T} \left[d\bar{E} + \left(\frac{\partial \ln Z}{\partial V} \right) dV - \mu d\bar{N} \right] \end{aligned}$$

To interpret the second term on the right-hand side of this equation, we compare the expression enclosed within the parenthesis with the statement of the first law of thermodynamics, viz.,

$$\delta Q = d\bar{E} + \delta W - \mu d\bar{N} \quad (2.3.20)$$

We immediately identify $(\partial \ln Z / \partial V) dV$ as δW , the work done by the system.

$$\therefore \frac{\delta Q}{T} = d \left[k \left\{ \ln Z - \frac{\bar{N}\mu}{kT} + \frac{\bar{E}}{kT} \right\} \right].$$

The quantity $\left[k \left\{ \ln Z - \frac{\bar{N}\mu}{kT} + \frac{\bar{E}}{kT} \right\} \right]$ is identified with the entropy S of the system. Accordingly,

$$S = \left[k \left\{ \ln Z - \frac{\bar{N}\mu}{kT} + \frac{\bar{E}}{kT} \right\} \right]$$

$$\Rightarrow \ln Z = \frac{S}{k} + \frac{\bar{N}\mu}{kT} - \frac{\bar{E}}{kT} = \frac{TS + \bar{N}\mu - \bar{E}}{kT}$$

But $\bar{N}\mu = G$, the Gibbs free energy of the system [see Problem (2.46)]. Again G is equal to $(\bar{E} - TS + PV)$. So finally

$$P = \frac{kT}{V} \ln Z(\mu, V, T) \quad (2.3.21)$$

Thus, the grand canonical partition function directly gives the pressure as a function of μ, V and T .

4. Helmholtz free energy

The Helmholtz free energy is given by

$$F \equiv \bar{N}\mu - PV = \bar{N}kT \ln z - kT \ln Z(\mu, V, T)$$

where $z = e^{\mu\beta} \rightarrow$ fugacity.

$$F = -kT \ln \frac{Z(\mu, V, T)}{z^{\bar{N}}} \quad (2.3.22)$$

which can be compared with the canonical ensemble formula $F = -kT \ln Z(N, V, T)$.

5. Entropy

The entropy of the system is given by

$$S \equiv \frac{\bar{E} - F}{T} = kT \left(\frac{\partial \ln Z(\mu, V, T)}{\partial T} \right)_{\mu, V} + k \ln \frac{Z(\mu, V, T)}{z^{\bar{N}}}$$

$$\therefore S = kT \left[\frac{\partial \ln Z(\mu, V, T)}{\partial T} \right]_{\mu, V} + k \ln Z(\mu, V, T) - \bar{N}k\mu\beta \quad (2.3.23)$$

2.3.4 Equation of state

Eliminating μ between (2.3.19) and (2.3.21), one obtains the equation of state, i.e., the (P, V, T) -relationship.

PROBLEM 2.42: Show that

$$\text{(a)} \langle N \rangle = z \frac{\partial}{\partial z} \ln Z(z, V, T), \quad \text{(b)} \langle N^2 \rangle - \langle N \rangle^2 = z \frac{\partial}{\partial z} z \frac{\partial}{\partial z} \ln Z(z, V, T)$$

where $z = e^{\mu\beta}$, known as **fugacity**.

where $g(T, P)$ is independent of N_j .

$$\therefore \mu_j = \left(\frac{\partial G}{\partial N_j} \right)_{T, P} = g(T, P) = \frac{G}{N_j} \quad (\text{Proved}) \quad (\text{xi})$$

i.e., the chemical potential per molecule is just equal to the Gibbs free energy per molecule.

When several species are present, then $G = G(T, p, N_1, \dots, N_m)$ and in general

$$\mu_j = \left(\frac{\partial G}{\partial N_j} \right)_{T, P, \{N_1 \dots N_{i-1} \dots N_{i+1} \dots N_m\}} \neq \frac{G}{N_j}.$$

PROBLEM 2.44: Show that the entropy of a grand canonical ensemble can be written as

$$S = -k \sum_r P_r \ln P_r.$$

SOLUTION

The grand canonical partition function is

$$Z(\mu, V, T) = \sum_r e^{\mu \beta N_r - \beta E_r} \quad (\text{i})$$

and the probability of finding the system in the r th microstate is

$$P_r = \frac{e^{\mu \beta N_r - \beta E_r}}{\sum_r e^{\mu \beta N_r - \beta E_r}} = \frac{e^{\mu \beta N_r - \beta E_r}}{Z(\mu, V, T)} \quad (\text{ii})$$

$$\therefore \ln P_r = -\ln Z + \mu \beta N_r - \beta E_r$$

$$\Rightarrow \sum_r P_r \ln P_r = \frac{\sum_r P_r \ln P_r}{\sum_r P_r} = -\ln Z \frac{\sum_r P_r}{\sum_r P_r} + \mu \beta \frac{\sum_r N_r P_r}{\sum_r P_r} - \beta \frac{\sum_r E_r P_r}{\sum_r P_r}$$

$$\Rightarrow \sum_r P_r \ln P_r = \mu \beta \bar{N} - \beta \bar{E} - \ln Z \quad (\text{iii})$$

Let us now introduce a new variable $\alpha = \mu \beta$.

$$\therefore Z(\alpha, V, \beta) = \sum_r e^{\alpha N_r - \beta E_r} \quad (\text{iv})$$

Now

$$d \ln Z = \frac{\partial \ln Z}{\partial \alpha} d\alpha + \frac{\partial \ln Z}{\partial V} dV + \frac{\partial \ln Z}{\partial \beta} d\beta = \bar{N} d\alpha + \bar{p} \beta dV + \beta d\bar{E}$$

$$\Rightarrow d(\ln Z - \bar{N} \alpha + \bar{E} \beta) = -\alpha d\bar{N} + \bar{p} \beta dV + \beta d\bar{E}$$

$$\Rightarrow d(\ln Z - \bar{N} \alpha + \bar{E} \beta) = \beta \left[d\bar{E} + \bar{p} dV - \frac{\alpha}{\beta} d\bar{N} \right] = \beta [d\bar{E} + \bar{p} dV - \mu d\bar{N}]$$

But $TdS = d\bar{E} + \bar{p}dV - \mu d\bar{N}$.

$$\therefore d(\ln Z - \bar{N}\alpha + \bar{E}\beta) = \frac{dS}{k}$$

whence

$$\begin{aligned} \frac{S}{k} &= (\ln Z - \bar{N}\mu\beta + \bar{E}\beta) \\ \Rightarrow \ln Z &= \frac{S}{k} + \bar{N}\mu\beta - \bar{E}\beta \end{aligned} \quad (v)$$

Using (v) in (iii), we finally get

$$S = -k \sum_r P_r \ln P_r \quad (\text{Proved}) \quad (vi)$$

PROBLEM 2.45: Using $S = -k \sum_r P_r \ln P_r$, show that for a grand canonical ensemble, $TdS = d\bar{E} + \bar{p}dV - \mu d\bar{N}$.

SOLUTION

We know that

$$S = -k \sum_r P_r \ln P_r \quad (i)$$

Now

$$P_r = \frac{e^{\mu\beta N_r - \beta E_r}}{Z(\mu, V, T)} \Rightarrow \ln P_r = \mu\beta N_r - \beta E_r - \ln Z \quad (ii)$$

Using (ii) in (i)

$$\begin{aligned} S &= -k \left[\mu\beta \sum_r P_r N_r - \beta \sum_r P_r E_r - \ln Z \sum_r P_r \right] \\ &= -k [\mu\beta\bar{N} - \beta\bar{E} - \ln Z] \left(\because \sum_r P_r = 1, \sum_r P_r E_r = \bar{E}, \sum_r P_r N_r = \bar{N} \right) \\ &= k \ln Z + k\beta\bar{E} - k\mu\beta\bar{N} \\ \Rightarrow dS &= k \frac{\partial \ln Z}{\partial \mu} d\mu + k \frac{\partial \ln Z}{\partial V} dV + k \frac{\partial \ln Z}{\partial T} dT + k\beta d\bar{E} + k\bar{E} d\beta - k\beta\mu d\bar{N} - k\beta\bar{N} d\mu - k\mu\bar{N} d\beta \\ &= k\beta\bar{N} d\mu + k\beta\bar{p}dV + k\mu\bar{N} d\beta - k\bar{E} d\beta + k\beta d\bar{E} + k\bar{E} d\beta - k\beta\mu d\bar{N} - k\beta\bar{N} d\mu - k\mu\bar{N} d\beta \\ &\quad \left(\because \frac{\partial \ln Z}{\partial T} dT = \frac{\partial \ln Z}{\partial \beta} d\beta, \frac{\partial \ln Z}{\partial \mu} = \beta\bar{N}, \frac{\partial \ln Z}{\partial V} = \beta\bar{p}, \frac{\partial \ln Z}{\partial \beta} = \mu\bar{N} - \bar{E} \right) \\ &= k\beta d\bar{E} + k\beta\bar{p}dV - k\beta\mu d\bar{N} \\ \Rightarrow TdS &= d\bar{E} + \bar{p}dV - \mu d\bar{N} \quad \left(\because \beta = \frac{1}{kT} \right) \end{aligned}$$

Taking logarithms on both sides

$$\ln Z(\mu, V, T) = \sum_{i=1}^{\alpha} \ln Z\left(\mu, \frac{V}{\alpha}, T\right) = \alpha \cdot \ln Z\left(\mu, \frac{V}{\alpha}, T\right)$$

$$\Rightarrow \ln Z\left(\mu, \frac{V}{\alpha}, T\right) = \frac{1}{\alpha} \cdot \ln Z(\mu V, T)$$

This shows that $\ln Z(\mu, V, T)$ is linear in V .

PROBLEM 2.47: Show that $Z(\mu, V, T) = e^{\bar{N}}$ for an ideal gas, if the gas molecules are treated as indistinguishable.

SOLUTION

The grand canonical partition function is $Z(\mu, V, T) = \sum_r e^{\mu\beta N_r - \beta E_r}$. We can write this partition function in another form:

$$Z(\mu, V, T) = \sum_{Nr} e^{\mu\beta N - \beta E_{Nr}} = \sum_{Nr} e^{\mu\beta N} e^{-\beta E_{Nr}} = \sum_{N=0}^{\infty} e^{\mu\beta N} Z(N, V, T)$$

where $Z(N, V, T) = \sum_r e^{-\beta E_{Nr}} \rightarrow$ canonical partition function.

For an ideal gas, the canonical partition function is $Z(N, V, T) = \xi^N$, where ξ is the single particle canonical partition function and is given by $\xi = \frac{V}{h^3} \left(\frac{2\pi m}{\beta}\right)^{3/2}$.

$$\therefore Z(\mu, V, T) = \sum_{N=0}^{\infty} e^{\mu\beta N} \xi^N \quad (\text{i})$$

If the gas molecules are treated as indistinguishable, then $N!$ permutations of the molecules among themselves do not lead to physically distinct situations and hence equation (i) must be divided by $N!$.

$$\therefore Z(\mu, V, T) = \frac{\sum_{N=0}^{\infty} e^{\mu\beta N} \xi^N}{N!} = \frac{\sum_{N=0}^{\infty} (e^{\mu\beta \xi})^N}{N!} = \exp\left(e^{\mu\beta \xi}\right) \quad (\text{ii})$$

Again, we know that

$$\bar{N} = \frac{1}{\beta} \frac{\partial \ln Z(\mu, V, T)}{\partial \mu} = \frac{1}{\beta} \left(\frac{\partial (e^{\mu\beta \xi})}{\partial \mu} \right) = e^{\mu\beta \xi}. \quad (\text{iii})$$

Using (iii) in (ii)

$$Z(\mu, V, T) = e^{\bar{N}} \quad (\text{Proved})$$

PROBLEM 2.48: Consider a system of N molecules in a container of volume V . Assuming that there is no correlation whatsoever between the locations of the various molecules, calculate the probability that a region of volume v contains exactly n molecules.

SOLUTION

The probability that the region of volume v exactly contains n molecules is given by

$$P_n = \frac{\sum_r e^{\mu\beta n - \beta E_{nr}}}{Z(\mu, v, T)} = \frac{e^{\mu\beta n} \sum_r e^{-\beta E_{nr}}}{Z(\mu, v, T)} = \frac{e^{\mu\beta n} Z(n, v, T)}{Z(\mu, v, T)} \quad (\text{i})$$

where $Z(n, v, T) =$ canonical partition function $= \xi^n / n!$, ξ being the single particle canonical partition function. $n!$ appears because of the essential indistinguishability of the particles. Again, from problem 2.50, $\bar{n} = e^{\mu\beta} \xi$ and $Z(\mu, v, T) = e^{\bar{n}}$.

$\therefore P_n = \frac{(e^{\mu\beta} \xi)^n / n!}{e^{\bar{n}}} = \frac{(\bar{n})^n}{n!} e^{-\bar{n}}$. This is known as **Poisson's distribution**.

PROBLEM 2.49: Consider a system of N molecules forming a substance which consists of two phases. The whole system is isolated so that its total energy E and its total volume V are both fixed. Find the necessary conditions for equilibrium between the two phases.

SOLUTION

Let the two phases be 1 and 2. The whole system is isolated, so that its total energy E , its total volume V and its total number of particles N are fixed. Let N_i be the number of molecules of the substance in phase i and denote the energy of this phase by E_i and its volume by V_i .

Then we must have the conservation conditions:

$$E_1 + E_2 = E = \text{constant}$$

$$\Rightarrow dE_1 = -dE_2 \quad (\text{i})$$

$$V_1 + V_2 = V = \text{constant}$$

$$\Rightarrow dV_1 = -dV_2 \quad (\text{ii})$$

$$N_1 + N_2 = N = \text{constant}$$

$$\Rightarrow dN_1 = -dN_2 \quad (\text{iii})$$

The equilibrium condition corresponds to the most probable situation, i.e., when the thermodynamic probability Ω is maximum. But $S = k \ln \Omega$. Hence, the equilibrium condition is that the entropy is maximum, i.e.,

$$S = S(E_1, V_1, N_1; E_2, V_2, N_2) = \text{maximum} \quad (\text{iv})$$

Again $S = S_1(E_1, V_1, N_1) + S_2(E_2, V_2, N_2)$.

Thus, the maximum condition (iv) yields

$$dS = dS_1 + dS_2 = 0 \quad (\text{v})$$

Now $S_1 = S_1(E_1, V_1, N_1)$.

$$\therefore dS_1 = \left(\frac{\partial S_1}{\partial E_1} \right)_{V_1, N_1} dE_1 + \left(\frac{\partial S_1}{\partial V_1} \right)_{E_1, N_1} dV_1 + \left(\frac{\partial S_1}{\partial N_1} \right)_{E_1, V_1} dN_1 \quad (\text{vi})$$

In a simple case, when the number N_1 is fixed, the fundamental thermodynamic relation asserts that

$$dS_1 = \frac{1}{T_1} (dE_1 + p_1 dV_1) \quad (\text{vii})$$

where T_1 and p_1 are respectively the temperature and mean pressure of phase 1. Under this circumstance, $dN_1 = 0$. A comparison of the coefficients of dE and dV in (vi) and (vii) yields

$$\left(\frac{\partial S_1}{\partial E_1}\right)_{V_1, N_1} = \frac{1}{T_1} \quad (\text{viii})$$

$$\left(\frac{\partial S_1}{\partial V_1}\right)_{E_1, N_1} = \frac{p_1}{T_1} \quad (\text{ix})$$

Let $\mu_1 = -T_1 \left(\frac{\partial S_1}{\partial N_1}\right)_{E_1, V_1}$. The quantity μ_1 is the chemical potential per molecule in phase 1.

Then (vi) can be written in the form

$$dS_1 = \frac{1}{T_1} dE_1 + \frac{p_1}{T_1} dV_1 - \frac{\mu_1}{T_1} dN_1 \quad (\text{x})$$

Similarly,

$$dS_2 = \frac{1}{T_2} dE_2 + \frac{p_2}{T_2} dV_2 - \frac{\mu_2}{T_2} dN_2 = -\frac{1}{T_2} dE_1 - \frac{p_2}{T_2} dV_1 + \frac{\mu_2}{T_2} dN_1 \quad (\text{xi})$$

Using (x) and (xi) in (v)

$$\left(\frac{1}{T_1} - \frac{1}{T_2}\right) dE_1 + \left(\frac{p_1}{T_1} - \frac{p_2}{T_2}\right) dV_1 - \left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2}\right) dN_1 = 0 \quad (\text{xii})$$

Since (xii) is to be valid for arbitrary variations dE_1, dV_1, dN_1 , it follows that the coefficients of all these differentials must vanish separately. Thus, one obtains

$$\left(\frac{1}{T_1} - \frac{1}{T_2}\right) = 0$$

$$\left(\frac{p_1}{T_1} - \frac{p_2}{T_2}\right) = 0$$

$$\left(\frac{\mu_1}{T_1} - \frac{\mu_2}{T_2}\right) = 0$$

whence

$$T_1 = T_2 \quad (\text{xiii})$$

$$p_1 = p_2 \quad (\text{xiv})$$

$$\mu_1 = \mu_2 \quad (\text{xv})$$

These are the necessary conditions for equilibrium between two phases. (xiii) is the condition for **thermal equilibrium**, (xiv) for **mechanical equilibrium** and (xv) for **diffusive equilibrium**.

where \vec{v} is 2f-dimensional velocity of the representative points and \hat{n} is a unit vector, outward normal to the point of location of the surface element ds of the surface s , enclosing the volume τ and $d\tau = dq_1 \dots dq_f dp_1 \dots dp_f$.

Applying Gauss' divergence theorem

$$\oint_s \rho \vec{v} \cdot \hat{n} ds = \int_\tau \vec{\nabla} \cdot (\rho \vec{v}) d\tau \quad (2.5.3)$$

Using (2.5.3) in (2.5.2)

$$\int_\tau \left[\frac{\partial \rho}{\partial t} + \vec{\nabla} \cdot (\rho \vec{v}) \right] d\tau = 0. \text{ Since } \tau \text{ is arbitrary,}$$

$$\frac{\partial \rho}{\partial t} + \vec{\nabla} \cdot (\rho \vec{v}) = 0 \quad (2.5.4)$$

This is the well-known equation of continuity and is a statement of the conservation of density in phase space. Here $\vec{\nabla}$ is a 2f-dimensional del operator.

The second term of (2.5.4) can be written as

$$\begin{aligned} \vec{\nabla} \cdot (\rho \vec{v}) &= \sum_{i=1}^f \left[\frac{\partial}{\partial q_i} (\rho \dot{q}_i) + \frac{\partial}{\partial p_i} (\rho \dot{p}_i) \right] \\ &= \rho \sum_{i=1}^f \left[\frac{\partial \dot{q}_i}{\partial q_i} + \frac{\partial \dot{p}_i}{\partial p_i} \right] + \sum_{i=1}^f \left[\frac{\partial \rho}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial p_i} \dot{p}_i \right] \end{aligned} \quad (2.5.5)$$

In view of the Hamilton's equation (2.5.1), the first term is

$$\sum_{i=1}^f \left[\frac{\partial^2 H}{\partial q_i \partial p_i} - \frac{\partial^2 H}{\partial p_i \partial q_i} \right] = 0$$

\therefore Equation (2.5.4) takes the final form

$$\frac{\partial \rho}{\partial t} + \sum_{i=1}^f \left[\frac{\partial \rho}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial p_i} \dot{p}_i \right] = 0 \quad (2.5.6)$$

Again using Hamilton's equation (2.5.1), we can put (2.5.6) in another form:

$$\frac{\partial \rho}{\partial t} + \sum_{i=1}^f \left[\frac{\partial \rho}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial \rho}{\partial p_i} \frac{\partial H}{\partial q_i} \right] = 0$$

$$\Rightarrow \frac{\partial \rho}{\partial t} + [\rho, H] = 0 \quad (2.5.7)$$

where $[\rho, H] = \sum_{i=1}^f \left[\frac{\partial \rho}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial \rho}{\partial p_i} \frac{\partial H}{\partial q_i} \right]$, the Poisson bracket.

Since ρ is a function of q 's, p 's and t , the left-hand side is the total time derivative, $\frac{d\rho}{dt}$.

$$\therefore \boxed{\frac{\partial \rho}{\partial t} = \frac{d\rho}{dt} + [\rho, H] = 0} \quad (2.5.8)$$

This is known as **Liouville's** equation.

Thus, $\rho(q_1, \dots, q_f, p_1, \dots, p_f, t)$ remains constant along the dynamic trajectories, i.e., the lines whose parametric equations $q_i = q_i(t)$, $p_i = p_i(t)$ are derived from the equations of motion (2.5.1), in Γ -space. This is known as Liouville's theorem.

2.5.1 Statistical equilibrium

To get an equilibrium distribution, we need

$$\frac{\partial \rho}{\partial t} = 0 \quad (2.5.9)$$

which immediately implies that

$$\frac{\partial \rho}{\partial q_i} \dot{q}_i + \frac{\partial \rho}{\partial p_i} \dot{p}_i = 0 \quad (2.5.10)$$

Using the Hamilton's equation (2.5.1)

$$\frac{\partial \rho}{\partial q_i} \frac{\partial H}{\partial p_i} - \frac{\partial \rho}{\partial p_i} \frac{\partial H}{\partial q_i} = 0 \quad (2.5.11)$$

which is easily satisfied, if we take

$$\rho(q_i, p_i) = \rho(H(q_i, p_i)) \quad (2.5.12)$$

because then

$$\frac{\partial \rho}{\partial q_i} \frac{\partial H}{\partial p_i} = 0 \text{ and } \frac{\partial \rho}{\partial p_i} \frac{\partial H}{\partial q_i} = 0$$

Thus, there is a restriction (2.5.12) on the equilibrium distribution. In other words, the equilibrium distribution corresponds to the situation where ρ is constant on surfaces of constant energy H in phase space. This is indeed the basic assumption of statistical mechanics.

QUESTIONS

1. Give the concept of ensemble.
2. What do you mean by microcanonical ensemble? For what type of system is it suitable?
3. Show that $\Omega(E) \sim E^f$, i.e., $\Omega(E)$ is a rapidly increasing function of the energy E of the system.
4. Discuss the specific heat behaviour of a two-level system. What is Schottky anomaly?
5. What do you mean by canonical ensemble? For what type of system is it suitable?
6. For a canonical system, derive the Boltzmann's canonical probability distribution law, $p_r = \frac{e^{-\beta E_r}}{\sum_r e^{-\beta E_r}}$ where $\beta = \frac{1}{kT}$.
7. What is partition function? What is its importance in statistical mechanics?
8. Show that the energy fluctuation in a canonical system is proportional to $\frac{1}{\sqrt{N}}$
9. How can you justify the equivalence between a microcanonical ensemble and a canonical ensemble?

3. Consider a system of N particles at a temperature T . Each particle has mass m and free to execute one-dimensional simple harmonic motion about its mean position. If the restoring force is proportional to x , calculate the specific heat of the system. Assume that the temperature T is high enough so that classical statistics is applicable.
4. Find the canonical distribution function for a body rotating with angular velocity.
5. Suppose that two atoms interact with the mutual potential energy of the form $U(x) = U_0 \left[\left(\frac{a}{x} \right)^{12} - 2 \left(\frac{a}{x} \right)^6 \right]$, where x is the separation between the two particles. The particles are in contact with a heat reservoir at an absolute temperature T such that $kT \ll U_0$, but high enough so that classical statistics is applicable. Calculate the mean separation $\bar{x}(T)$ of the particles and use it to compute the expansion coefficient $\alpha = \frac{1}{\bar{x}} \frac{\partial \bar{x}}{\partial T}$.